NASA CR-111889

DEMONSTRATION OF A STERILIZABLE SOLID ROCKET MOTOR SYSTEM

Contract NAS1-10086

FINAL REPORT

JANUARY 1971

D. O. DePree

Aerojet Solid Propulsion Company
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TABLE OF CONTENTS

LIST OF FIGURES

SUMMARY

This successful demonstration of the heat sterilization of case-bonded, insulated and lined solid rocket strain motors was made possible by a careful analysis of the chemical, physical and mechanical problems imposed by heat sterilization. The demonstration provides the basis for design, fabrication, sterilization and testing of full-scale motors.

Each of the motor components previously developed specifically for the heat sterilization application was tested both individually and in composite systems. On the basis of a stress analysis derived from a full characterization of the propellant and propellant-liner-insulation bond, a grain configuration and strain levels were selected for the strain motor demonstration. Three strain levels were selected, (1) a level at which failure would be anticipated, (2) a strain level believed to be marginal and (3) a strain level projected to survive. In addition to these motors a motor having a stress relief liner-insulation was designed and fabricated as a back-up configuration.

After six heat sterilization cycles consisting of 53 hrs per cycle at a grain temperature of 135°C (275°F) the stress relieved grain and one of the lower strain level grains remained in excellent condition. A second low strain level grain failed in strain after five sterilization cycles. Radiographic and visual examination of the bond interface indicated the propellant and bond at the interface to be in excellent condition after sterilization. All failures occurred in strain by the formation of cracks initiating at the inner bore.

INTRODUCTION

This is the final report submitted in fulfillment of the requirements of the National Aeronautics and Space Administration Contract NAS1-10086.

Availability of heat sterilizable solid motors would significantly aid the design engineer in planning space missions where entry of a space vehicle into a biologically quarantined area is required. Sterilizable solid rockets could find application in deorbiting operations, gas generators and many other special applications. Although a considerable effort has been expended by various aerospace industries as well as government laboratories, no successful demonstration of the heat sterilizability of a realistic insulated case-bonded solid rocket motor system had been achieved prior to the current study.[1][2] It was the purpose of the present effort, therefore, to demonstrate that subscale motors comprising the total rocket motor system, i.e. case, insulation, liner and propellant could successfully survive six heat sterilization cycles without adversely affecting motor integrity. This successful demonstration lays the basis for design fabrication, sterilization and firing of full-scale motors as final proof of solid rocket motor sterilization capability.

The approach to heat sterilization taken at Aerojet is that all of the components of the solid rocket motor, the case, the insulation, the liner and the propellant must not only be stable independently to heat sterilization but must not interact with each other in such a way as to degrade other components. Thus, the chemical stability of each of the composite components is the first consideration because thermal degradation is in essence a chemical process and the reactions involved have a direct bearing not only on the components themselves but through migratory processes on neighboring materials.

The approach therefore comprised a chemical analysis of the problem, development of chemical techniques and a basis of material selection to assure stable components. Applying this background to the current program, the individual components were evaluated separately and as composites, under heat sterilization conditions. The selected materials were then fully characterized mechanically to provide a basis for realistic stress analysis. On the basis of the stress analysis a set of subscale strain motor grains was designed and cast and the capability of the total motor system to survive heat sterilization demonstrated.

TECHNICAL DISCUSSION

A. MOTOR COMPONENT SELECTION

As previously indicated the severe environment and extreme cycling conditions imposed upon a solid rocket motor by heat sterilization (six 53 hr heat treatments at 135°C (275°F)) demand that the various rocket components be chemically stable at high temperatures and possess physical, mechanical and bonding properties adequate to survive the severe temperature changes imposed by thermal cycling.

Studies conducted at Aerojet under company-sponsorship since 1964 have demonstrated that certain state-of-the-art case materials and insulations are available which will meet the heat sterilization requirement. However, these same studies showed state-of-the-art propellants were not adequate to meet the high temperature requirements and that liners as conventionally formulated and processed did not provide high temperature bond stability. These studies led to the development of a highly stable, heat sterilizable propellant and liner system which when used with a conventional case and insulation provided the basis for heat sterilizability.

The following paragraphs describe the basis for selecting the components for the demonstration program and present the mechanical, ballistic and physical properties of the various motor materials.

Propellant Selection - The propellant selected for the demonstration program was ANB-3289-2, a non-plasticized, saturated HTPB propellant containing stabilized ammonium perchlorate. This propellant may be formulated either in an aluminum-containing or non-aluminum containing version. The propellant composition, as well as the thermodynamic, ballistic, physical, and mechanical properties of the aluminum-containing version selected for this sterilization demonstration program are summarized in Figure 1.

Elimination of aluminum from the formulation would not affect the capability of the propellant to withstand heat sterilization but would reduce the expected standard specific impulse of the propellant and increase the minimum obtainable burning rate.

The effect of solids composition (84 to 86 wt%) on the expected standard specific impulse of the aluminum-containing version of ANB-3289-2 is shown in Figure 2. Processing considerations limit the solids loading to 85% with an expected standard specific impulse at 18% aluminum of 2380 N-sec/Kg (242.6 lbf-sec/lbm). The effect of solids composition on the standard specific impulse of the non-aluminum-containing version is shown in Figure 3. Satisfactory processing of the non-aluminum propellant can be achieved at a solid loading of 83% with an expected standard specific impulse of 2230 N-sec/Kg (227 lbf-sec/lbm).

The excellent stability of ANB-3289-2 propellant under heat sterilization conditions has been demonstrated by subjecting 3 x 3 x 5 inch blocks to six 53 hour exposures at 135°C in air. Evidence of lack of degradation and gassing is offered by the fact that dimensions of the propellant blocks were essentially

ANB-3289-2 PROPELLANT
(Composition, Thermodynamic, Ballistic, Physical and Mechanical Properties)

A. COMPOSITION

Ingredient	Weight %
Ammonium Perchlorate (Stabilized with 0.5% FC-169) (Grind Composition Ung/HSMP(1) = 80/20	67.000
Aluminum H-5	18.000
DC-200 Antifoaming Agent	0.005
FC-154 Bonding Agent; Telagen-S Binder; Trimethylolpropane (TMP) } (2); Dimer Acid Diisocyanate (DDI)	14.995
Total	100.000

B. THERMODYNAMIC PROPERTIES

Specific Impulse
(Expected Standard) = 242.6 sec. (242.6 lbf-sec/lbm)

Mass Flow Coefficient, C_w
(Theoretical) = 0.00062 Kg/N-sec (0.00617 lbm/lbf-sec)

Thrust Coefficient, C_f = 1.632

Exhaust Velocity, C* = 1590 m/sec (5217 ft/sec)

Isentropic Flow Coefficient
Theoretical (Shifting equil.) = 1.1327
Effective = 1.20

Chamber Flame Temperature
(Theoretical) = 3084°C (5534°F)

Exhaust Flame Temperature
(Theoretical) = 1774°C (3226°F)

(1) Unground/high-speed Mikropulverizer ground.

(2) Ratio adjusted to provide desired properties.

ANB-3289-2 PROPELLANT (Cont.)

B. Thermodynamic Properties (Cont.)

Ave. Molecular Weight of Gases

Chamber	= 27.069 g/mol.
Exhaust	= 27.714 g/mol

Heat of Formation =-41.775 Kcal./100g.

Oxygen Balance

$\bar{O} - \bar{C}$	= 1.2789 g atoms/100g.
$\bar{O} - (\bar{C} + 1.5\ \overline{Al})$	= 0.2778 g atoms/100g.

C. THEORETICAL EQUILIBRIUM EXHAUST COMPOSITION

Product	Product Quantity, moles/100g: Chamber at 3084°C (5584°F)	Product Quantity, moles/100g: Exhaust at 1774°C (3226°F)
HCl	0.4247	0.5674
N_2	0.2940	0.2944
H_2O	0.3416	0.2435
H_2	1.3701	1.4583
O_2	0.0001	-
O	0.0006	-
OH	0.0126	0.0001
Cl	0.0244	0.0015
NO	0.0008	-
H	0.1149	0.0051
NH_3	0.0001	-
CO	1.0057	1.0023
CO_2	0.0316	0.0351
HCN	0.0001	-

ANB-3289-2 PROPELLANT (Cont.)

C. Theoretical Equilibrium Exhaust Composition (Cont.)

Product	Product Quantity, moles/100g: Chamber at 3084°C (5584°F)	Exhaust at 1774°C (3226°F)
SiO	0.0001	0.0001
Al	0.0006	-
AlH	0.0001	-
AlCl	0.0239	-
$AlCl_2$	0.0471	0.0006
$AlCl_3$	0.0010	0.0001
AlO	0.0002	-
Al_2O	0.0001	-
AlOCl	0.0001	-
Al_2O_3	0.2971	0.3334

D. BALLISTIC PROPERTIES

Burning Rate (Solid Strand) (26.7°C)

138 N/cm^2 (200 psi)	=	0.28 cm/sec (0.11 in./sec)
552 N/cm^2 (800 psi)	=	0.43 cm/sec (0.17 in./sec)
Pressure Exponent	=	0.32
cp^n (26.7°C, 138-552 N/cm^2)	=	$0.015\ p^{0.36}$

E. MECHANICAL PROPERTIES

Test Temp. °C	(°F)	σ_m N/cm^2	(psi)	ε_m %	ε_o %	E_o N/cm^2	(psi)
-18	(0)	504	(730)	8	10	10626	(15400)
4.4	(40)	186	(270)	14	22	2477	(3590)
25	(77)	115	(167)	13	15	1387	(2010)
43	(110)	95	(138)	11	12	1318	(1910)
66	(150)	75	(108)	9	10	1118	(1620)
93	(200)	60	(87)	7	8	1007	(1460)
135	(275)	43	(62)	5	7	994	(1440)

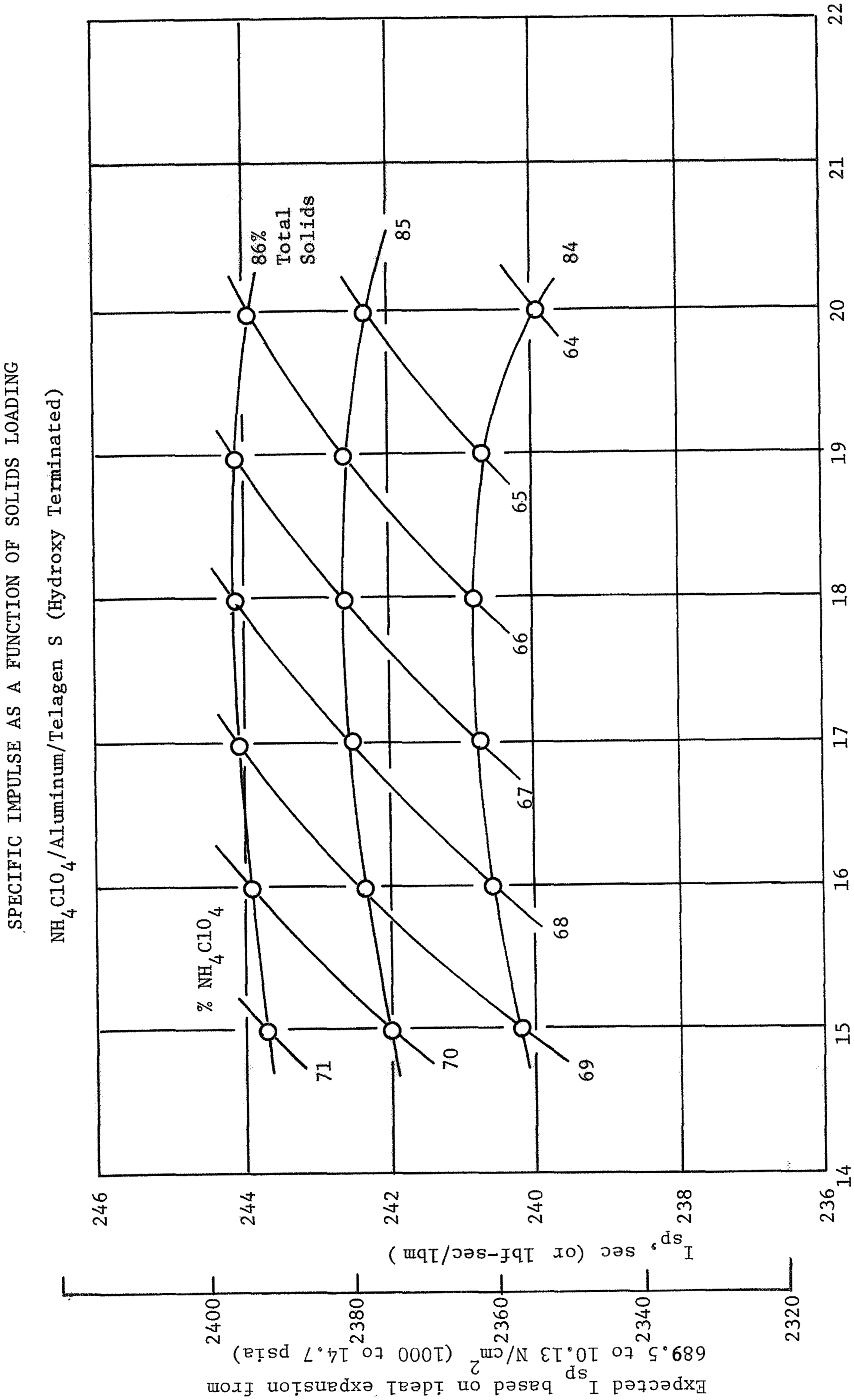

SPECIFIC IMPULSE AS A FUNCTION OF SOLIDS LOADING
NH_4ClO_4/Aluminum/Telagen S (Hydroxy Terminated)
86% Total Solids
85
84
% NH_4ClO_4
71
70
69
68
67
66
65
64
14
15
16
17
18
19
20
21
22
wt. % Aluminum
246
244
242
240
238
236
I_{sp}, sec (or lbf-sec/lbm)
2400
2380
2360
2340
2320
Expected I_{sp} based on ideal expansion from
689.5 to 10.13 N/cm^2 (1000 to 14.7 psia)

Figure 2

SPECIFIC IMPULSE OF NON-ALUMINIZED PROPELLANT
(ANB-3289 Binder)

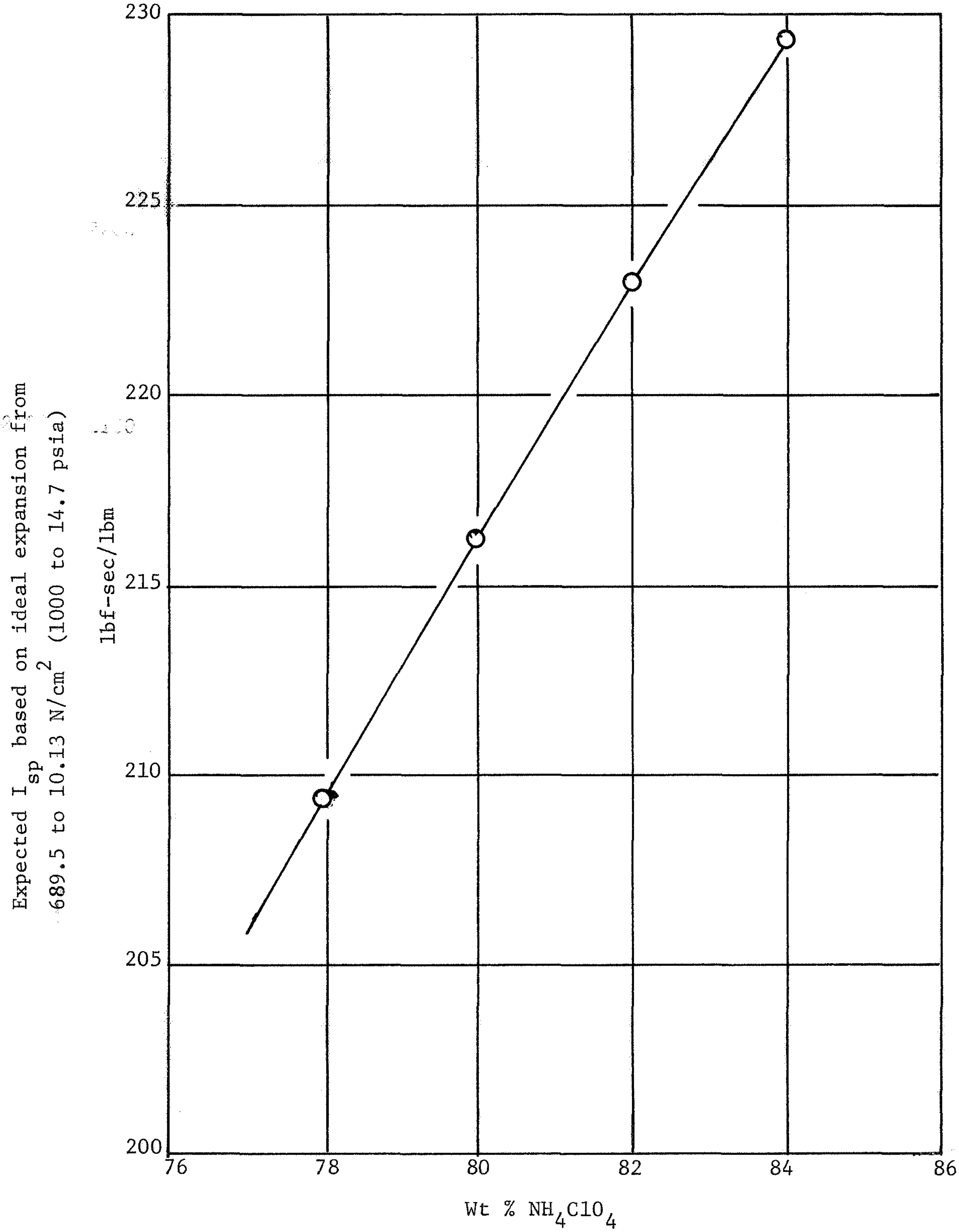


Figure 3

unchanged by the heat treatment (Figure 4). Oxidative degradation is essentially nil as indicated by an increase in the surface hardness of only six Shore A units and a weight loss of only 0.07 wt% (Figure 4). Conclusive evidence of propellant stability is illustrated by the data presented in Figure 5 which shows only a small change in propellant mechanical properties occurred during six heat cycles. In addition, the mechanical properties of specimens taken from the center of the block were identical to those taken from the surface.

Basis for Propellant Selection - ANB-3289-2 propellant was developed specifically to provide a high performance propellant which would meet the space storage and heat sterilization requirements of this type program. The composition and processing methods were the result of assessment of the conditions imposed by the space environment and heat sterilization treatment. The critical factors associated with meeting these requirements were isolated (1) through studies of the stability of propellant ingredients and the interaction of these ingredients by differential thermal analysis, (2) small specimen sterilization tests, and (3) confirmation of heat sterilization capability and processing techniques by sterilization and testing of propellant blocks.

Aerojet Solid Propulsion Company has been working on the development of solid propellant capable of operation after dry heat sterilization since late 1964. In initial studies, attempts were made to adapt state-of-the-art propellants to the sterilization application. These tests conducted with free standing grains formulated from propellant AN-583AF were marginally successful when tested according to the sterilization requirements imposed at that time (3, 36 hr cycles at 145°C (293°F)). With the desire for higher performance case bonded grains and the introduction of a more severe sterilization qualification requirement (6, 53 hr cycles at 135° C (275°F)), it was found that no off-the-shelf propellants would

PHYSICAL CHANGES DURING 275°F HEAT STERILIZATION CYCLING OF ANB-3289-2 PROPELLANT

(4000g Batch No. 10LR-3563, 7.5 x 7.5 x 12.5 cm)

			No. of 53 hr Cycles at 135°C (275°F) Dimensions in cm				
Block No.	Dimension Location (1)	Initial	1	3	4	5	6
1	1	12.720	12.728	12.705	12.725	12.720	12.720
	2	6.421	6.429	6.421	6.426	6.421	6.419
	3	6.317	6.317	6.312	6.312	6.309	6.299
	4	6.330	6.332	6.317	6.325	6.335	6.317
2	1	11.140	11.140	11.133	11.143	11.143	11.140
	2	7.620	7.615	7.615	7.612	7.615	7.615
	3	7.569	7.569	7.587	7.554	7.551	7.544
	4	7.569	7.557	7.557	7.567	7.564	7.549
			Weight Change, Wt%				
1		---	0.000	0.023	0.034	0.045	0.068
2		---	0.000	0.027	0.036	0.046	0.073
			Surface Hardness, Shore A				
		64	70	72	71	71	70

(1) Dimension Location

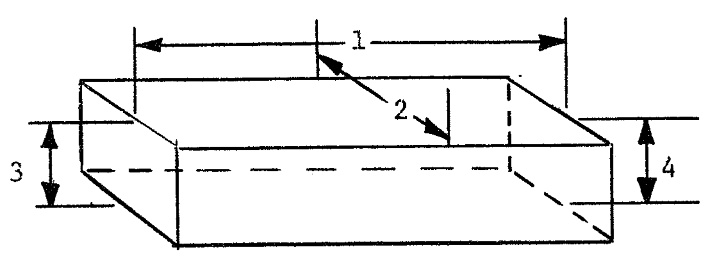


Figure 4

EFFECT OF HEAT STERILIZATION* ON THE MECHANICAL PROPERTIES OF ANB-3289-2 PROPELLANT

Batch No.	History	Specimen Location	Mechanical Properties at 25°C (77°F)					
			σ_m		ε_m, %	ε_b, %	E_o	
			N/cm^2	(psi)			N/cm^2	(psi)
10LR-3563	Initial	---	94	(136)	21	33	1179	(1708)
	Heat Sterilized	Surface	70	(102)	24	44	918	(1330)
	Heat Sterilized	Center	72	(104)	23	45	900	(1305)

* Six 53 hr exposures to 135°C (275°F) in air as measured by thermocouple placed 2.5 cm (1 in.) below propellant surface.

Figure 5

successfully withstand heat sterilization. In the course of these studies it was shown that both the oxidizer and binder must be considered in the development of thermally stable solid propellants.

Recognizing the limitations of off-the-shelf propellants, studies were conducted to isolate the problem areas and develop a high performance case-bonded propellant based on stabilized ammonium perchlorate and a non-plasticized saturated hydrocarbon binder which shows no change in ballistic properties and little change in mechanical properties after heat sterilization. In Appendix A, the studies leading to the formulation of propellant for space storage and heat sterilization are discussed. Because of their significance, the thermal stability of ammonium perchlorate and the stabilization techniques are discussed first, followed by a discussion of the importance of binder high temperature stability studies and propellant processing considerations. These studies led to the development of the heat sterilizable propellant ANB-3289-2 while continuing studies have provided heat sterilizable insulations and bonding systems for use with this propellant in case-bonded motor configurations.

Self-heating during heat sterilization will not pose a hazard with ANB-3289-2 based on self-heating tests with a similar propellant. These tests show that web thicknesses of greater than 25.4 cm (10-in.) can be heated at 135°C (275°F) without encountering exothermic reaction rates sufficient to heat the grain to autoignition temperature.

Safety tests show the impact sensitivity of ANB-3289-2 propellant to be 15 cm (2Kg weight) and the propellant could not be ignited under standard tests in the rotary friction test.

Insulation Selection - Liner-bond integrity is of prime importance in any case bonded motor. To ensure bond integrity the total bond system consisting of motor case/insulation/liner/propellant had to be considered. Migration of volatile or mobile species from any of the individual components in this composite bond system can seriously affect bond integrity. Since temperature increases the mobility of such species and accelerates decomposition reactions with possible formation of undesirable contaminants, selection of bond systems suitable for heat sterilization required a careful analysis of the behavior of each component and assurance that no interactions would occur that could adversely affect the bond.

These company-sponsored studies showed that maximum resistance to oxidative attack during the long high temperature exposure imposed by heat sterilization, as in the case of the propellant binder, is achieved by elimination of sites subject to oxidative attack. Of the materials tested the most stable, both from the standpoint of mechanical properties and bonding characteristics was GenGard V-4030 insulation, (an ethylene propylene rubber) containing no reactive migratory components. Nevertheless this insulation as indicated later does undergo a significant change in mechanical properties during heat sterilization.

Liner Selection - Because the stability of the propellant/liner bond is a critical factor to the success of the motor sterilization program, preliminary tests were made to optimize bonding techniques to assure the most stable bond system. These studies, which were initiated before the contract was awarded, indicated that an extremely stable bond can be achieved if certain precautions in liner selection and treatment are followed.

Previous studies conducted at Aerojet in which a variety of liners were evaluated for stability to heat sterilization showed that the presence of a cure catalyst resulted in degradation of the propellant interface and, in fact, in some instances caused considerable degradation of the liner itself. This observation, which is similar to the one previously made that the propellant itself must be free of catalysts, required the selection of a bonding system from which catalysts could be eliminated.

This requirement would appear to impose a severe restriction on the liner formulation because it is highly desirable that the liner gel rapidly so that precise control of liner thickness can be assured and catalysts are needed to provide rapid gelation and cure. The problem, however, was overcome by the selection of a liner containing a volatile amine catalyst which can be removed from the liner after cure. The liner selected, SD-886, has been shown to provide excellent propellant bonds which are essentially unaffected by heat sterilization. SD-886 liner contains a binder based on a polyestertriol, diepoxide-diisocyanate curing agents, an amine catalyst and TiO_2 and carbon black fillers.

The preliminary tests to optimize the liner application, cure and catalyst stripping were conducted using double plate tensile (DPT) specimens. These specimens were prepared with 1.52 mm (60 mil) thick GenGard V-4030 insulation because the catalyst could be absorbed into the insulation and then later diffuse into the bond interface.

Two sets of DPT specimens were prepared, in both sets the insulation was bonded to the steel plates with Chemlock 220 adhesive and 205 metal primer.

The insulated plates were given a 24 hr heat soak at 149°C (300°F) to remove any volatile species and decompose any filler hydrates. The first set was then lined with SD-886 liner and given the standard 43°C (110°F) cure for 48 hrs. The second set was lined, given the standard cure, and then given a 24 hr soak at 149°C (300°F) to remove any absorbed amine catalyst from the insulation. Both DPT sets were then spatula cast with ANB-3289-2 propellant and cured at 57°C (135°F) for ten days. The mechanical properties of the 4.54 Kg (10-lb) propellant batch are shown below:

σ_m, N/cm^2(psi)	σ_b, N/cm^2(psi)	ε_m, %	ε_b, %	E_o, N/cm^2(psi)
90 (130)	73(106)	33	50	522 (756)

The two sets of DPT specimens were then subjected to heat sterilization. The first set, 8 specimens, permitted testing after each of seven 60 hr cycles. The second, given a 149°C bake, contained 7 specimens and therefore could only be tested after each of six cycles. The tensile data obtained are shown in Figure 6.

The data presented confirm the excellent bonding properties and thermal stability of the SD-886/ANB-3289-2 bond. That the standard cure treatment is not adequate to remove all of the amine catalyst is indicated by the poorer bond and gummy interface exhibited by the initial bond tensile. With heat sterilization the catalyst apparently is volatilized and the bond became comparable to the heat treated set. In a motor, however, volatilization would be far more difficult and therefore the heat treatment would be required. Some slight loss in strength of the propellant itself is indicated over the six to seven heat sterilization cycles. This is probably due to the fact that the modulus of the propellant is low enough to permit some fatiguing to occur.

Peel specimens comprised of GenGard 4030 insulation (2.5 x 10 cm (1 x 4 in) specimens), SD-886 liner and ANB-3289-2 propellant having a crosslinker concentration of 35 equivalents were prepared. The peel specimens were made up with GenGard 4030

EFFECT OF HEAT STERILIZATION ON THE TENSILE STRENGTH
OF ANB-3289-2 PROPELLANT SD-886 LINER BOND

(DPT Specimens Insulated with GenGard 4030 EPR Insulation[1])

	Bond Tensile, at 25°C			
	Standard SD-886 Cure		Standard Cure + 24 hrs Bake at 149°C (300°F)	
No. of Sterilization Cycles[2]	N/cm^2	(psi)	N/cm^2	(psi)
0	87	(126)[3]	100	(145)[4]
1	97	(140)[4]	100	(145)[4]
2	99	(143)[5]	90	(130)[5]
3	93	(135)[5]	91	(132)[5]
4	92	(134)[5]	92	(134)[5]
5	92	(133)[5]	90	(130)[5]
6	93	(135)[5]	95	(137)[5]
7	85	(123)[5]		

(1) Insulation bonded to plates with Chemlock 220, vulcanized for 1-1/2 hrs at 149°C during bond cure, then given an additional 24 hrs bake at 149°C.
(2) Heat sterilization cycle 60 hrs at 135°C.
(3) Failure close to bond interface, some clean peel, propellant at interfaces softened.
(4) Failure in propellant near bond interface, normal propellant at bond interface.
(5) Failure in propellant, normal propellant at bond interface.

Figure 6

insulation rather than glass cloth in order to more closely approximate actual motor conditions. This was considered important in that migratory species under heat sterilization conditions would adversely affect the peel strength of either the insulation/liner or the liner propellant bond. The techniques developed for minimizing volatile ingredients and eliminating the liner cure catalyst reported in the previous paragraphs were followed. The insulation was given a 24 hr bake at 149°C (300°F) prior to liner application and the cured lined specimens a 24 hr bake at 149°C (300°F) prior to propellant casting.

The peel strength of the bond was determined at 25°C (77°F) both initially and after two, four and six heat sterilization cycles. As shown by the data presented in Figure 7, the peel strength is $\sim$5.7 N/cm^2 (8 psi). Heat sterilization does not affect the peel strength of the liner/propellant bond and failure occurs in the propellant close to the liner/propellant interface.

Materials - In a previous Aerojet sterilization study the following inert materials were tested to determine the effects of heat sterilization:

Test Material or Specimen	Type of Tests
Fiberglass-epoxy (filament wound chamber materials)	Weight loss, hardness, composite tensile strength, and horizontal shear strength
Aluminum	Tensile, fracture toughness, and stress corrosion properties
Silica-phenolic (nozzle insulation material)	Weight loss, hardness, flatwise tensile strength, edgewise compressive strength, interlaminar shear strength, and regression rate
O-ring material: Buna N, Viton, silicone, and ethylene propylene	Hardness, weight loss, compression set, tear resistance, tensile strength, and elongation
Fiberglass-epoxy to GenGard V-45 and SD-850 insulation bond	Lap shear strength at ambient and elevated temperatures

EFFECT OF HEAT STERILIZATION ON THE PEEL STRENGTH OF THE ANB-3289-2 PROPELLANT/SD-886 LINER BOND

(Peel Specimens 2.5 x 2.5 x 10 cm GenGard-4030 Insulation/SD-886 Liner/ANB-3289-2 Propellant)

No. of Sterilization Cycles[1]	Peel Strength at 25°C[2] (77°F) N/cm^2	(psi)	Nature of Failure
0	4.8	(7.0)	CPI[3]
2	5.9	(8.5)	CPI
4	5.7	(8.2)	CPI
6	5.7	(8.2)	CPI

(1) 1 cycle = 53 hrs at 135°C
(2) Strain rate 50.8 cm/min
(3) Cohesive failure in propellant near bond interface

Figure 7

Material specimens were heat sterilized in a nitrogen atmosphere and the material properties were measured by standard procedures. Control specimens were also prepared, stored at ambient condition, and tested to obtain comparative data. Two sets of sterilization conditions were used during the programs. Specimens were exposed to heat sterilization during the first test series only and to chemical decontamination and heat sterilization during the second test series. The conditions for the first series of tests were three 50-hr cycles at a temperature of 149°C (300°F). The conditions for the second series of tests were one 25-hr exposure to a 12% ethylene oxide - 88% Freon 12 atmosphere at a temperature of 50°C (122°F) followed by six 53-hr cycles at a temperature of 135°C (275°F). The results of these tests are summarized in Figures 8 through 11.

Because these tests show aluminum to be little affected by heat sterilization, 7 cm (2.75 inch) diameter motor casings (aluminum) were selected for use in the demonstration program. Although nozzles, igniters, and O-ring sealed joints were not required for the present study, the tests on these materials indicate that no problem exists in sterilizing these components. Data from tests of FM-5131, a typical silica-phenolic nozzle insulation material, indicate that the change in regression rate as measured in plasma arc tests (Figure 10) is the only effect of sterilization other than thermal expansion that will require consideration during motor design efforts.

Although the results of O-ring material tests (Figure 11) show that all materials are affected by sterilization, the property changes are not sufficient to prevent the O-rings from functioning satisfactorily.

EFFECTS OF STERILIZATION ON THE PROPERTIES OF
FILAMENT WOUND CHAMBER FIBERGLASS-EPOXY COMPOSITES

Material Specimen	Material Property					
	Horizontal Shear Strength		Composite Tensile Strength		Fiber Strength	
	N/cm^2	(psi)	N/cm^2	(psi)	N/cm^2	(psi)
Control	8459	(12,260)	125,580	(182,000)	175,467	(254,300)
Sterilized	9091	(13,175)	125,235	(181,500)	174,570	(253,000)
Change, %		+7.5		-0.27		-0.51
Control	7224	(10,469)	140,580	(203,740)	230,460	(334,000)
Sterilized(2)(3)	7304	(10,585)	145,106	(210,298)	237,878	(344,750)
Change, %		+1.08		+3.22		+3.22
Sterilized(2)(4)	7302	(10,583	143,948	(208,620)	235,980	(342,000)
Change, %		+1.08		+2.39		+2.39

(1) Sterilization conditions consisted of three cycles of 50 hr ea at 149°C (300°F).
(2) Sterilization conditions consisted of exposure to 12% ethylene oxide-88% Freon mixture at 50°C (122°F) for 25 hr and six cycles of 53 hr ea at 135°C (275°F) in a nitrogen atmosphere.
(3) Specimens exposed to sterilization environments in the presence of 7075 T6 aluminum.
(4) Specimens exposed to sterilization environments in the presence of 6Al-4V titanium.

Figure 8

EFFECTS OF STERILIZATION ON THE PROPERTIES
OF 7079-T6 ALUMINUM

Material Property	Material Specimen Control	Sterilized[1]	Change, %
Fracture Toughness:			
Pre-Cracked Charpy Tests,			
W/A cm-Kg/cm^2	9.72	11.04	
($in.-lb/in.^2$)	(54.3)	(61.7)	+13.6
Single Edge Notch Tests,			
K_{I_C}, N/cm^2-cm	4.79	5.44	
(ksi-in.)	(17.6)	(20.0)	+12.0
Tensile Properties:			
Yield Strength, N/m^2	4.09	4.04	
(ksi)	(59.4)	(58.6)	-1.35
Tensile Strength, N/m^2	5.15	4.95	
(ksi)	(74.6)	(71.8)	-3.75
Elongation, % (2.54 cm, 1.0 in.)	5.7	11.8	+107
Area Reduction, %	10.1	22.7	+125
Stress Corrosion:			
Yield Strength, 0.2% offset,			
N/m^2	3.82	3.91	
(ksi)	(55.4)	(56.7)	+2.34
Tensile Strength, N/m^2	4.71	4.80	
(ksi)	(68.3)	(69.6)	+1.90
Elongation, % (1.27 cm, 0.5 in.)	4.6	6.8	+47.8
Area Reduction, %	9.2	18.1	+96.7

(1) Sterilization conditions consisted of exposure to 12% ethylene oxide-88%, Freon mixture at 50°C (122°F) for 25 hr and six cycles of 53 hr ea at 135°C (275°F) in a nitrogen atmosphere.

Figure 9

EFFECTS OF STERILIZATION ON PROPERTIES OF SILICA PHENOLIC MATERIAL FM-5131

	Tensile Strength		Compressive Strength		Interlaminar Shear Strength		Plasma Arc Regression Rate (6)	
	N/cm^2	(psi)	N/cm^2	(psi)	N/cm^2	(psi)	cm/sec	(in./sec)
Control	4706	(6821)	18,630	(27,000)	553	(802) (5)	0.00195	(0.00077)
Sterilized (1)	5207	(7546)	18,044	(26,150)	541	(784) (5)	0.00279	(0.0011)
Change, %		+10.6		-3.14		-2.25		+42.9
Control	6935	(10,050)	12,989	(18,825)	1211	(1755)	0.00889	(0.0035)
Sterilized (2)(3)	7262	(10,525)	14,438	(20,925)	1256	(1820)	0.0104	(0.0041)
Change, %		+4.73		+11.2		+3.70		+17.1
Sterilized (2)(4)	7280	(10,550)	14,180	(20,550)	1283	(1860)	0.0117	(0.0046)
Change, %		+9.16		+9.16		+5.98		+31.4

(1) Sterilization conditions consisted of three cycles of 50 hr ea at 149°C (300°F).

(2) Sterilization conditions consisted of exposure to 12% ethylene oxide-88% Freon mixture at 50°C (122°F) for 25 hr and six cycles of 53 hr ea at 135°C (275°F) in a nitrogen atmosphere.

(3) Specimens exposed to sterilization environments in the presence of 7075 T6 aluminum.

(4) Specimens exposed to sterilization environments in the presence of 6Al-4V titanium.

(5) Specimens failed in tension, actual interlaminar shear strength is higher than value shown.

(6) Heat flux 11.36×10^3 joules/m^2-sec (500 Btu/ft^2-sec.).

Figure 10

EFFECTS OF STERILIZATION ON THE PROPERTIES OF O-RING MATERIALS

	Hardness, Shore "A"	Weight, gm	Compression Set %	Tear Resistance N/cm^2	Tear Resistance (psi)	Tensile Strength N/cm^2	Tensile Strength (psi)	Ultimate Elongation, %
Buna N								
Control	63	4.5311	31.1	168	(244)	1693	(2453)	397
Sterilized[1]	73	4.4138	20.3	183	(265)	1775	(2573)	247
Change, %	+11.6	-2.59	-34.7		+8.16		+4.89	-37.8
Viton								
Control	66	7.1869	46.4	141	(204)	1569	(2274)	267
Sterilized[1]	72	7.1770	37.4	124	(179)	1397	(2025)	250
Change, %	+9.09	-0.14	-19.4		-12.3		-10.9	-6.37
Silicone								
Control	53	4.7292	8.0	120	(174)	829	(1201)	503
Sterilized[1]	50	4.7237	9.5	102	(148)	789	(1143)	430
Change, %	-5.67	-0.12	+18.7		-14.9		-4.83	-23.6
Ethylene Propylene								
Control	73	5.5750	7.8	116	(168)	1334	(1933)	217
Sterilized[1]	75	5.5452	0.0	100	(145)	1263	(1830)	197
Change, %	+2.73	-0.53	-100		-13.7		-5.33	-9.22

(1) Sterilization conditions consisted of exposure to a 12% ethylene oxide-88% Freon mixture at 50°C (122°F) for 25 hr and six cycles of 53 hr ea at 135°C (275°F) in a nitrogen atmosphere.

Figure 11

Post-sterilization tests of titanium performed by Martin/Denver indicate that the metal is unaffected.

B. REQUALIFICATION OF RAW MATERIALS

Sufficient quantities of all of the raw materials required for the program were available from existing stock. The oxidizer, the metal to insulation adhesive, the insulation and the propellant binder and crosslinker were qualified through either chemical analysis and/or sterilization tests. Where required, additional purification steps were taken to assure the highest quality for these raw materials.

Oxidizer - Approximately 454 kg (1000 lbs) of stabilized ammonium perchlorate, prepared by the Pacific Engineering Company, has been kept in stock for approximately one year. This material, lot No. P.E. 69001, was ordered in anticipation of oxidizer needs for propellant sterilization programs. The material has been stored in sealed drums containing bags of desiccant.

This oxidizer was analyzed for moisture content and found to be extremely dry after the one year conditioning (surface moisture = 0.004 wt%, total moisture = 0.010 wt%). 9.08 Kg (20 lbs) of high speed Mikro-pulverizer ground (HSMP) oxidizer was prepared from this lot to provide the HSMP ground oxidizer for the program. The HSMP ground material was found to have a surface moisture of 0.010 wt% and total moisture content of 0.016 wt%.

Differential thermal analysis of both the unground and HSMP ground oxidizer indicated very satisfactory thermal stability. The thermographs obtained on 25 mg samples are shown in Figure 12 and compared with a thermograph of a typical unstabilized lot of ammonium perchlorate. The stabilized unground and ground oxidizers have essentially the same DTA's and show far smaller first exotherms then that for the unstabilized material. Stabilization has raised the onset of the first exotherm as predicted from 275 to 325°C.

Insulation and Metal to Insulation Adhesive - A sufficient quantity of GenGard 4030 EPR insulation was set aside to complete the program and provide sufficient insulation for one or two full-scale motors should scale-up at a later date be indicated. (GenGard 4030 insulation is free of processing aids and coatings.) A small sheet of the 1.52mm thick (60 mil) unvulcanized insulation was given a recommended 1.5 hr 149°C (300°F) vulcanization treatment under pressure and then cut into 12 micro Instron specimens. The effect of heat sterilization on the mechanical properties and weight loss of these specimens was determined and the results are presented in Figure 13. The insulation suffers an initial weight loss of approximately 1.5%, but little change in weight thereafter. This initial weight loss combined with a gain in mechanical properties during the first two heat sterilization cycles indicates the 1.5 hr vulcanization to be inadequate and that it is advisable to give insulated chambers at least one heat cycle prior to lining to insure full cure and removal of volatile ingredients. Although, surprisingly, the ethylene propylene rubber shows a considerable loss in mechanical properties during heat sterilization, the mechanical properties after sterilization are still far more than adequate to meet anticipated motor requirements.

The adequacy of the metal to insulation adhesive was also evaluated. The adhesive selected from previous studies was Chemlock 220 used with Chemlock 203 metal primer. Four 2.5 x 10 cm (1" x 4") aluminum strips were sanded and then primed with FM-47 primer. The FM-47 after cure was coated with Chemlock 203 primer.

DIFFERENTIAL THERMAL ANALYSIS OF GROUND AND UNGROUND
AMMONIUM PERCHLORATE (Lot # PE69001)

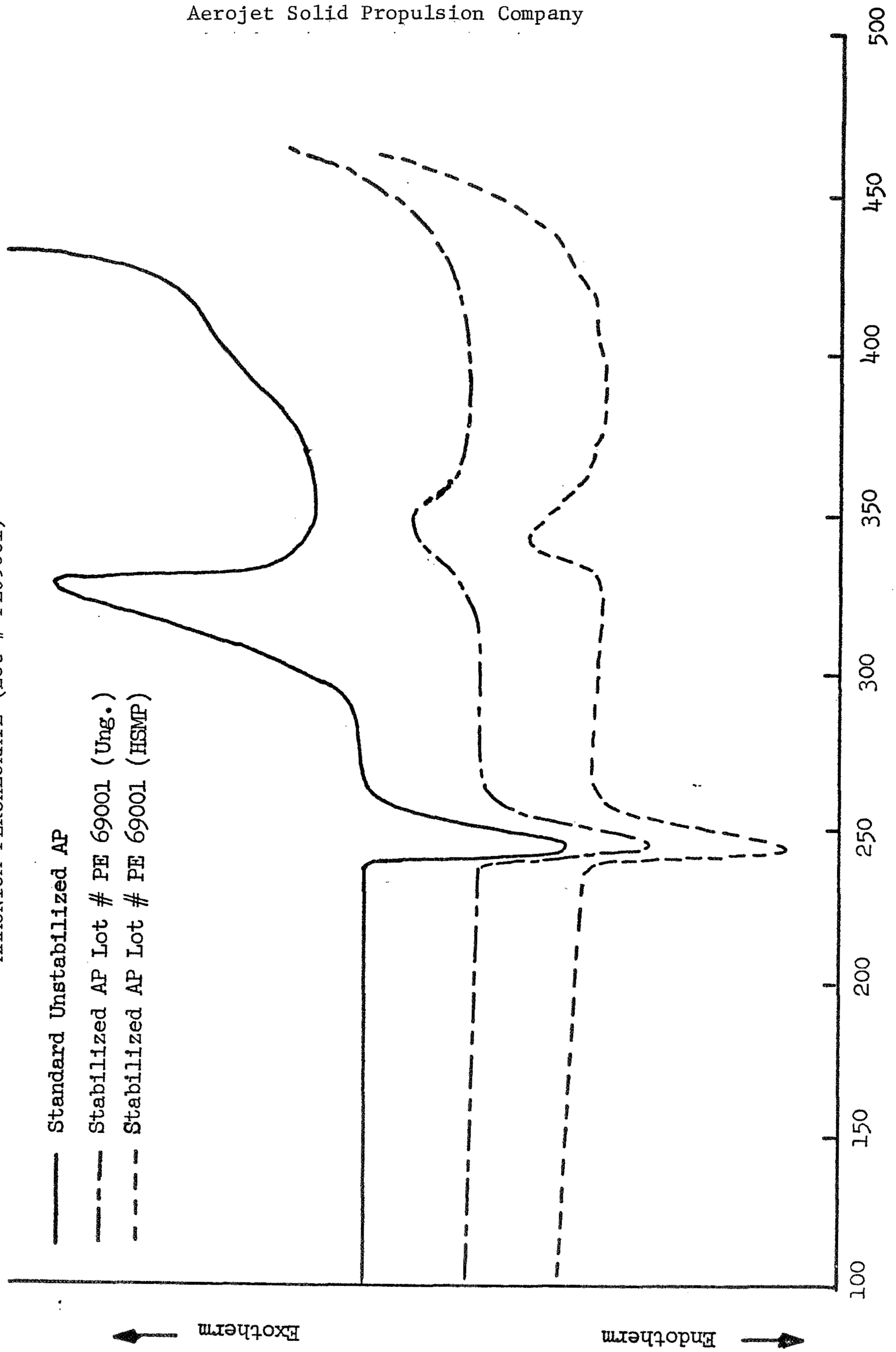


Figure 12

EFFECT OF HEAT STERILIZATION ON THE MECHANICAL PROPERTIES
AND WEIGHT LOSS OF GENGARD-4030 INSULATION

(Microtensile Specimens of Vulcanized(1) 1.52mm thick (60 mil) Insulation)

	Mechanical Properties(2) at 25°C (77°F) (Ave. of 3 Specimens)								
	σ_m		σ_b		ε_m	ε_b	E_o		
No. of Heat Sterilization Cycles(3)	N/cm^2	(psi)	N/cm^2	(psi)	%	%	N/cm^2	(psi)	Total Weight Loss, %(4)
0	566	(820)	491	(712)	214	258	2081	(3016)	-
2	844	(1223)	805	(1166)	227	257	4627	(6706)	1.55
4	789	(1144)	711	(1030)	131	150	5238	(7592)	1.73
6	932	(1351)	727	(1054)	55	83	5891	(8537)	2.08

(1) Vulcanization = 1.5 hr bake at 149°C (300°F).

(2) Measurements made in English units.

(3) 1 cycle = 60 hrs.

(4) Ave. of all remaining specimens.

Figure 13

Four 2.5 x 7.5 cm (1" x 3") specimens of GenGard 4030 insulation (unvulcanized) were abraded and coated on one surface with Chemlok 220 and the metal strips also coated with Chemlok 220. The specimens were bonded to the metal under 6.9 N/cm^2 (10 psi) pressure at 149°C (300°F) (1.5 hrs). The peel resistance of the specimens, as indicated by the Chemlok literature, is partially dependent on the pressure during vulcanization of the bond. The recommended pressure of 69 N/cm^2 (100 psi) was not available for the specimen preparation, hence, some variability in peel strength was observed. The bond was non-uniform with some surfaces found to bond extremely well while others had poorer bond strengths. Heat sterilization had little effect on the bond as indicated by manual testing. The weight loss of the bonded specimens, Figure 14, during heat sterilization was similar to that observed with the micro Instron specimens of GenGard 4030. Again a high temperature prebake at 135 to 149°C (275 to 300°F) for at least 24 hrs would be indicated. This is particularly important if the weight loss represents decomposition of hydrated fillers in the insulation.

Binder/Crosslinker - The Telagen-S (lot #316AM-5) purchased in 1969 for use in the preparation of heat sterilizable solid rocket propellants was specially prepared to provide a high concentration of bifunctional chains and reduced concentration of mono-functional or non-functional constituents which could lower the binder molecular weight and contribute migratory species and adverse bonding properties. The special treatment required to obtain this middle cut was chromatographic separation using a silica gel column. Analysis of the Telagen-S prepolymer for heavy metals indicated an iron content of ∿8 ppm and silicon of 150 ppm. The equivalent weight of the material as determined from the hydroxyl number was found to be 1080. The presence of heavy metals even in such low concentrations is not desirable because

WEIGHT LOSS OF ALUMINUM BONDED SPECIMENS OF GENGARD-4030 INSULATION

(2.5 x 7.5 cm strips of 1.52 mm thick insulation bonded with Chemlock 220 Adhesive to FM 47 and Chemlock 203 primed 2.5 x 10 cm aluminum strips)

	No. of Cycles at 135°C (275°F)(1)						
	0	2		4		6	
Specimen No.	weight,g	weight,g	loss,g(2)	weight,g	loss,g(2)	weight,g	loss,g(2)
1	14.6918	14.6071	0.0847	14.5942	0.0976	14.5851	0.1067
2	14.4942	14.4020	0.0922	14.3895	0.1047	14.3778	0.1164
3	14.6064	14.4892	0.1172	14.4780	0.1284	14.4672	0.1392
4	14.5952	14.5067	0.0885	14.4950	0.1002	14.4832	0.1120

(1) Heat cycle = 60 hrs

(2) Total loss in weight

Figure 14

of their catalytic effect on polymer decomposition. The trace of iron, though very small, could act as a primary catalyst. Silicon compounds have been found to be synergistic for iron.

The sources of the two comtaninants were presumed to be as follows:

a. Iron - iron oxide from corrosion of process equipment.

b. Silicon - silica gel used in chromatographic treatment of the polymer.

Experiments were conducted to determine the best technique for removing these impurities and it was found that treatment of the polymer in toluene solution with activated carbon (DARCO S-51RL, Atlas Chemical Industries) reduced the iron content to less than 2 ppm and the silicon to 27 ppm.

Using this technique, 5.45 Kg (12 lbs) of the Telagen-S prepolymer were treated in toluene solution. After treatment and careful filtration, the excess toluene was removed by flash distillation. The treated polymer was then thoroughly degassed by passage through a wiped film still at high vacuum at 200°C (392°F). Analysis of the treated polymers by emission spectroscopy showed complete elimination of all metal ions other than silicon, and reduction of the silicon content to 10 ppm. The equivalent weight of the polymer was found to be 1120 by hydroxyl analysis. The slight increase may be due to vacuum removal of lower molecular weight species. This very pure prepolymer was then set aside for use in the program.

The crosslinker, tri-methylolpropane (TMP), is a very pure commercial product purchased regularly by Aerojet Solid Propulsion Company. A total of 12.35 Kg (25 lbs) of Lot 6710 (eq. wt = 44) was set aside for use in this program. Additional testing was not undertaken.

A 17.25 Kg (38 lb) lot of the dimeryl-diisocyanate curing agent (Lot No. 8L306) was purchased from the Quaker Oats Co. in 1969 for the sterilization studies. This material was reanalyzed and found to have an equivalent weight of 306.

C. PROPELLANT MECHANICAL PROPERTIES ADJUSTMENT

As indicated previously a minimum crosslink density is required during heat sterilization of thick webs (>7.5 cm, 3.0 in.) if the development of propellant porosity is to be avoided. Previous tests had shown that a crosslink density in ANB-3289-2 propellant corresponding to a modulus of 1170 N/cm^2 (1700 psi) was adequate to overcome this type of fatiguing. It was therefore decided for the demonstration study that propellant with a modulus of 1380 N/cm^2 (2000 psi) would be used to assure elimination of fatigue and provide a margin of safety should differences in the functionality in the prepolymer from that previously tested affect the lower limit of stability.

Based on the experience with previous lots of Telagen-S saturated primary hydroxyl-terminated polybutadiene it was anticipated that the desired crosslink density to give a modulus of the order of 1380 N/cm^2 (2000 psi) would require 30 to 35 equivalents of trimethylolpropane. 4 Kg (10 lb) propellant qualification batches were therefore prepared at the two crosslinker levels. These batches completed cure as indicated by constant Shore "A" hardness readings in two weeks. The moduli of these batches 765 and 850 N/cm^2 (1109 and 1245 psi), respectively, fell below the desired 1380 N/cm^2 (2000 psi) modulus as shown in Figure 15. Assuming an approximately linear relationship between modulus and crosslinker concentration, a third 4 Kg (10 lb) batch was prepared using 50 equivalents of crosslinker. This propellant batch No. 10GP-1620 had a modulus of 2148 N/cm^2 (3113 psi) indicating a non-linear effect of crosslinker concentration on modulus at higher crosslink levels. Even at this high modulus the maximum elongation is still over 9%.

From a plot of the moduli of these three batches versus crosslinker concentration, Figure 16, a trimethylolpropane level of 43 equivalents was selected to obtain the desired modulus.

EFFECT OF CROSSLINKER CONCENTRATION ON THE MECHANICAL PROPERTIES OF ANB-3289-2 PROPELLANT

(4.54 kg (10-lb) Propellant Batches)

		Mechanical Properties at 25°C[2] (77°F)				
Batch No.	TMP, eq[1]	σ_m, N/cm^2 (psi)	σ_b, N/cm^2 (psi)	ε_m, %	ε_b, %	E_o, N/cm^2 (psi)
10GP-1559	30	98 (142)	84 (122)	27	38	765 (1109)
10GP-1564	35	110 (160)	106 (154)	23	27	859 (1245)
10GP-1620	50	125 (181)	118 (171)	9.3	12	2148 (3113)

(1) TMP = trimethylolpropane

(2) Strain rate = 4.42 cm/min (1.74 in/min)

Figure 15

EFFECT OF CROSSLINKER CONCENTRATION ON THE MODULUS OF ANB-3289-2 PROPELLANT

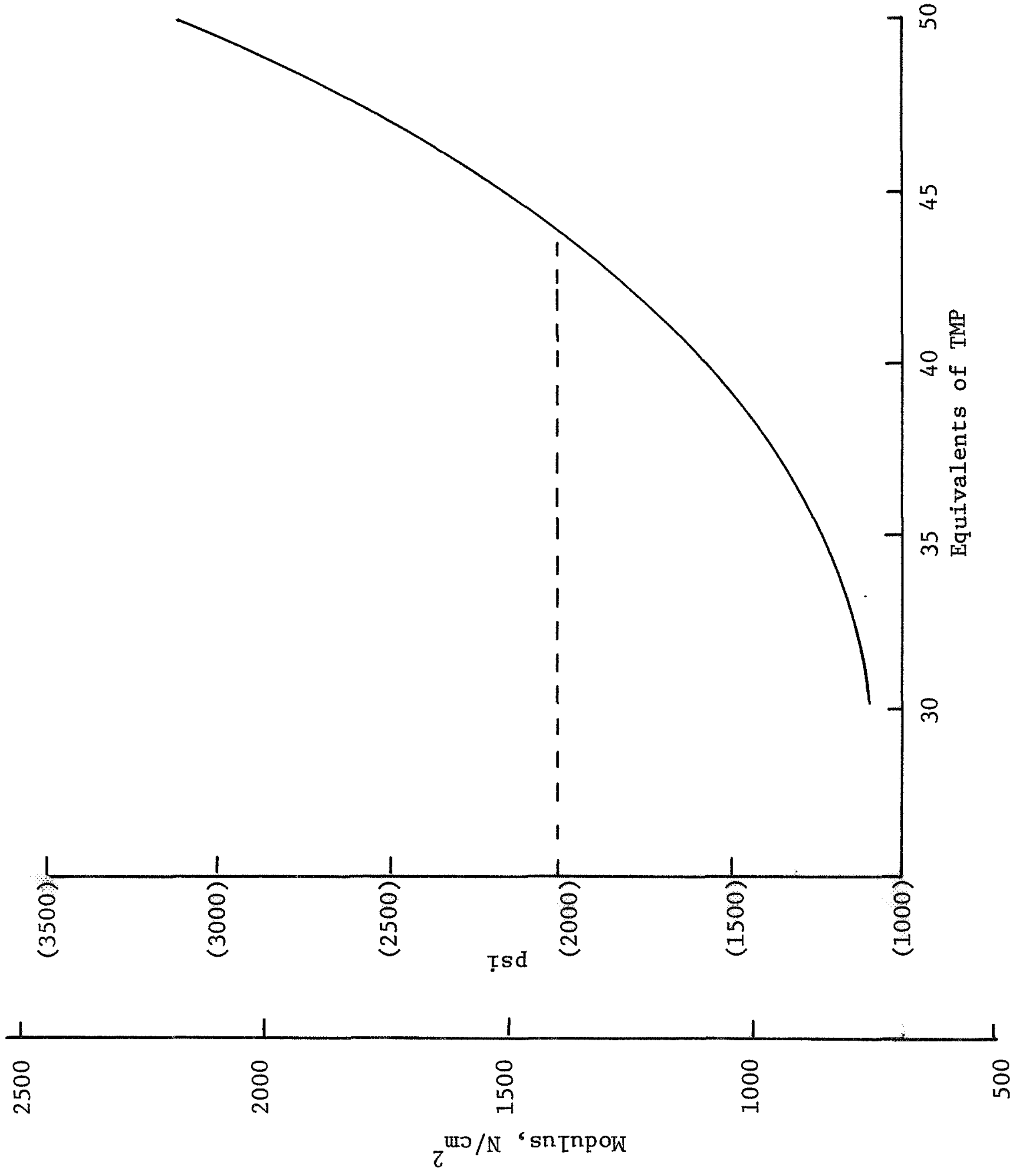


Figure 16

D. BURNING RATE

The solid strand burning rate of ANB-3289-2 propellant was determined from qualification batch No. 1620 over a pressure range of 140 to 550 N/cm^2 (200 to 800 psi). The plot of the data obtained is presented in Figure 17 and shows the propellant to have the desired low burning rate and a pressure exponent of 0.32.

E. MECHANICAL PROPERTIES AND BOND CHARACTERIZATION

Mechanical Properties - Propellant batches cast with 43 equivalents of crosslinker, the level indicated by the qualification batches had the desired propellant modulus of $\sim$1380 N/cm^2 (200 psi). Data showing the effect of strain rate and temperature on the uniaxial tensile properties of propellant prepared using the adjusted formulation are presented in Figure 18. These data show that the optimum elongation for the propellant occurs at 4.4°C (40°F). The tensile strength of the propellant at 135°C (275°F) was considered adequate as indicated by a tensile value of 43 N/cm^2 (62 psi) at a strain rate of 0.74 min^{-1} and 33 N/cm^2 (48 psi) at a strain rate of 0.074 min^{-1}.

The effect of strain rate on the uniaxial tensile properties of ANB-3289-2 under 217 N/cm^2 (300 psig) pressure was determined at 4.4 (40°F) and 25°C (77°F) to provide data for determination of allowables under motor firing conditions. These data are presented in Figure 19.

A plot of the strain rate data including measurements made at both ambient and 217 N/cm^2 (300 psig) pressure is presented in Figure 20.

A master relaxation curve for ANB-3289-2 propellant has been prepared based on measurements over the temperature range of -18 to 135°C (0-275°F). This curve which is presented in Figures 21A and 21B indicates an extremely low slope from -18°C (0°F) to a temperature of 93°C (200°F). At this point a discontinuity occurs indicating a greater drop off in relaxation modulus. This discontinuity is more apparent from the time-temperature shift plot presented in Figure 22. The lower

EFFECT OF PRESSURE ON THE BURNING RATE OF ANB-3289-2
PROPELLANT (80/20 Ung/ HSMP, Batch No. 10GP-1620)

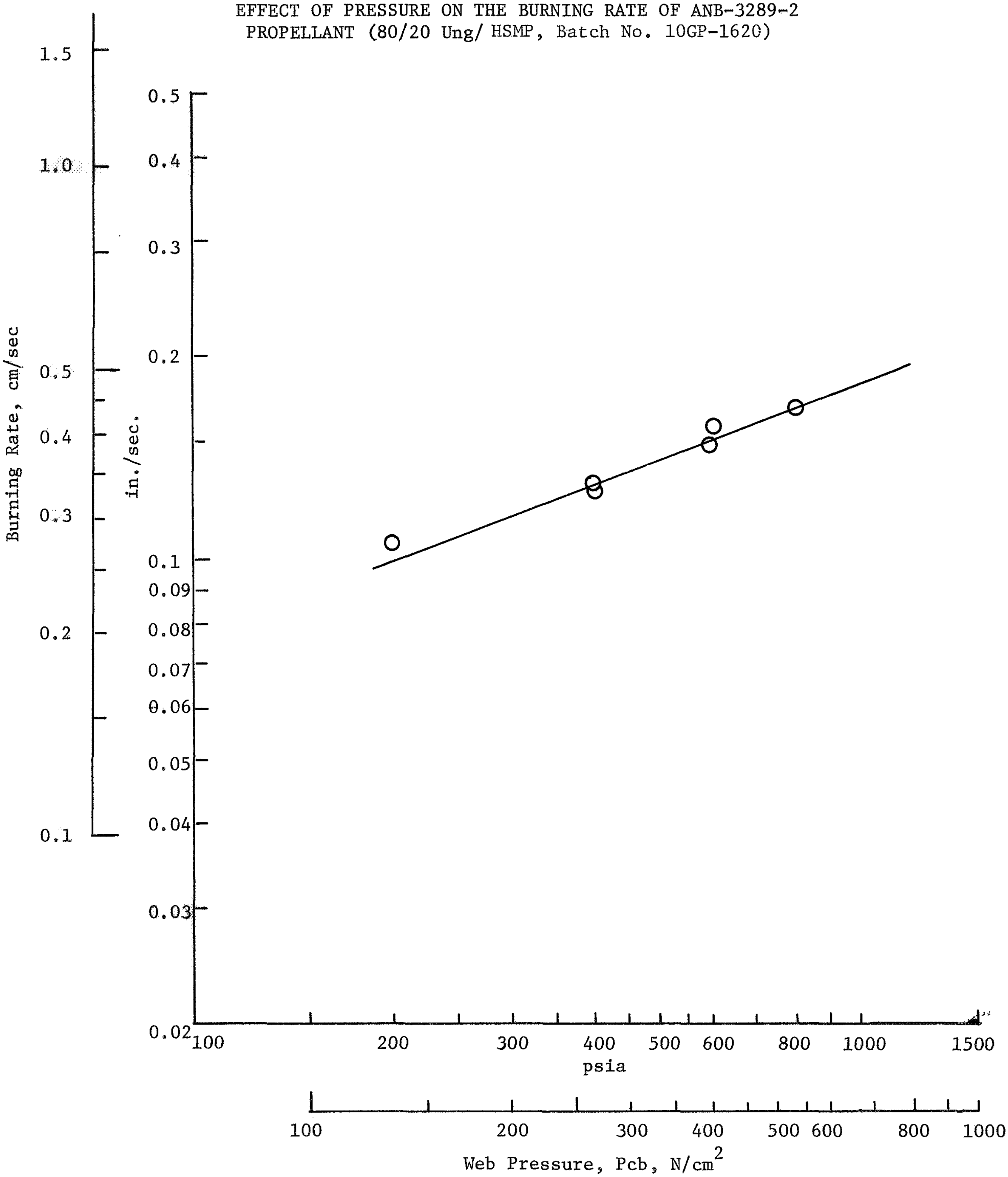


Figure 17

EFFECT OF TEST TEMPERATURE AND STRAIN RATE ON UNIAXIAL TENSILE PROPERTIES[1] ANB-3289-2 PROPELLANT: Batch 10GP-1685 (Heat Sterilizable Propellant)

Test Temp., °C	(°F)	Strain Rate, Min^{-1}	σ_m, N/cm^2	(psi)	ϵ_m %	ϵ_b %	E_o, N/cm^2	(psi)	Shore A Hardness
135	(275)	0.074	33	(48)	5.6	7.4	790	(1145)	
		0.74	43	(62)	5.1	7.0	996	(1444)	
93	(200)	0.074	46	(67)	6.6	7.6	882	(1278)	
		0.74	60	(87)	7.4	8.0	1006	(1458)	
66	(150)	0.074	61	(88)	7.0	7.8	1038	(1504) (2)	
		0.74	75	(108)	9.1	10.1	1119	(1622)	
43	(110)	0.074	73	(106)	9.2	11.8	1166	(1690)	
		0.74	95	(138)	10.7	11.9	1317	(1908)	78
25	(77)	0.074	88	(127)	12.0	13.8	1057	(1532)	79
		0.74	115	(167)	13.4	15.0	1386	(2009)	78
4.4	(40)	0.74	186	(270)	13.5	22.2	2474	(3586)	
-18	(0)	0.74	504	(731)	8.0	10.1	10612	(15379)	

(1) Mean value from 2 specimens tested at each condition.
(2) Value based on one specimen.

Figure 18

EFFECT OF TEST TEMPERATURE AND STRAIN RATE ON UNIAXIAL TENSILE PROPERTIES[1]
ANB-3289-2 PROPELLANT: Batch 10GP-1685

Test Temp., °C	(°F)	Strain Rate, min^{-1}	σ_m N/cm^2	(psi)	ε_m %	ε_b %	E_o N/cm^2	(psi)
25	(77)	10	219	(318)	21.7	26.3	1835	(2660)
		100	288	(417)	20.9	29.2	2881	(4175)
		1000	377	(547)	15.6	24.8	5941	(8610)
4.4	(40)	10	319	(462)	15.5	21.4	4406	(6385)
		100	435	(631)	15.3	23.3	5910	(8565)
		1000	655	(949)	10.4	17.0	14042	(20350)

(1) Mean value from 2 specimens tested at each condition.

EFFECT OF TEMPERATURE, STRAIN RATE, AND PRESSURE ON INITIAL TANGENT MODULUS: ANB-3289-2 PROPELLANT
Batch 10GP-1685

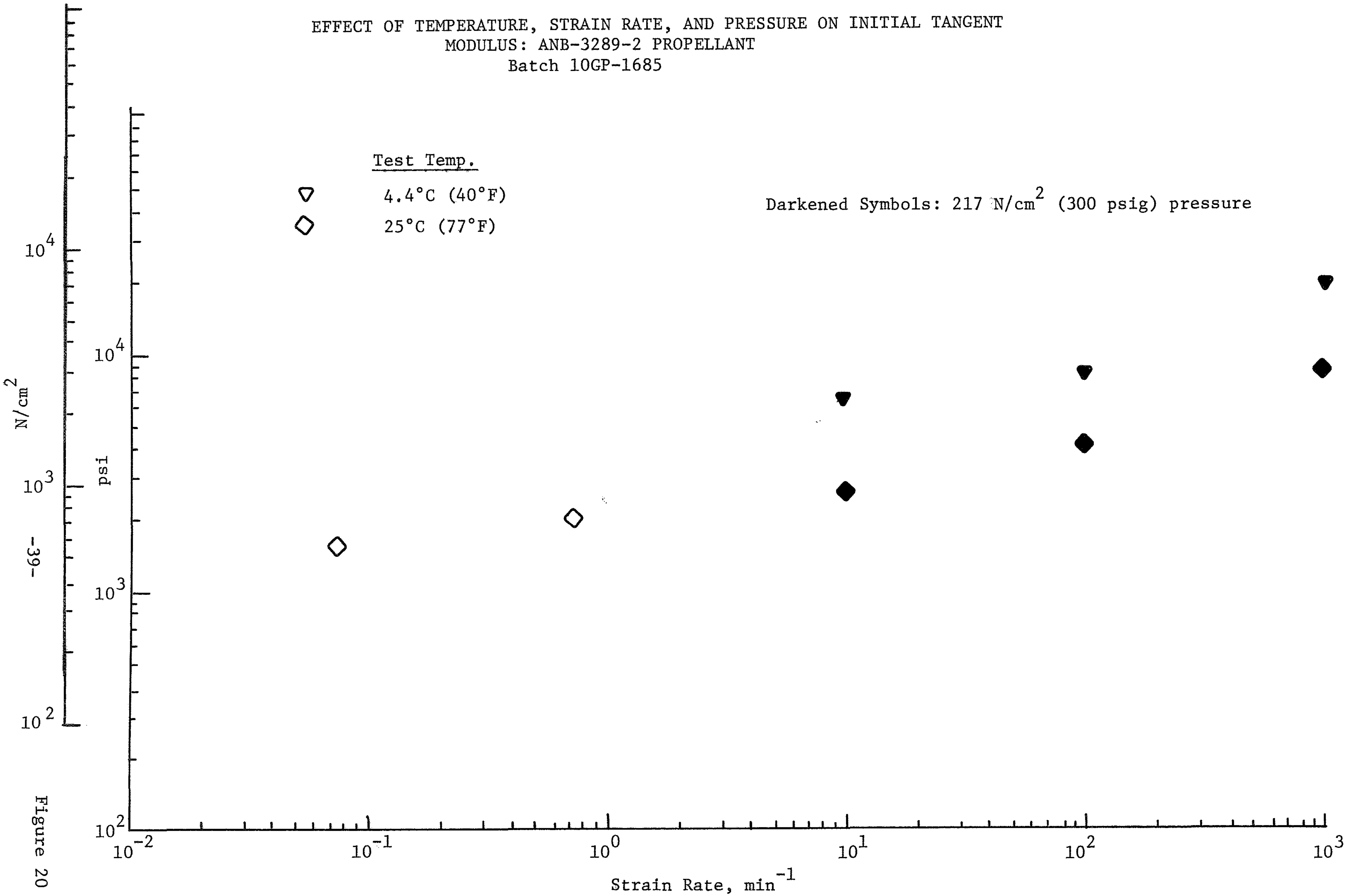
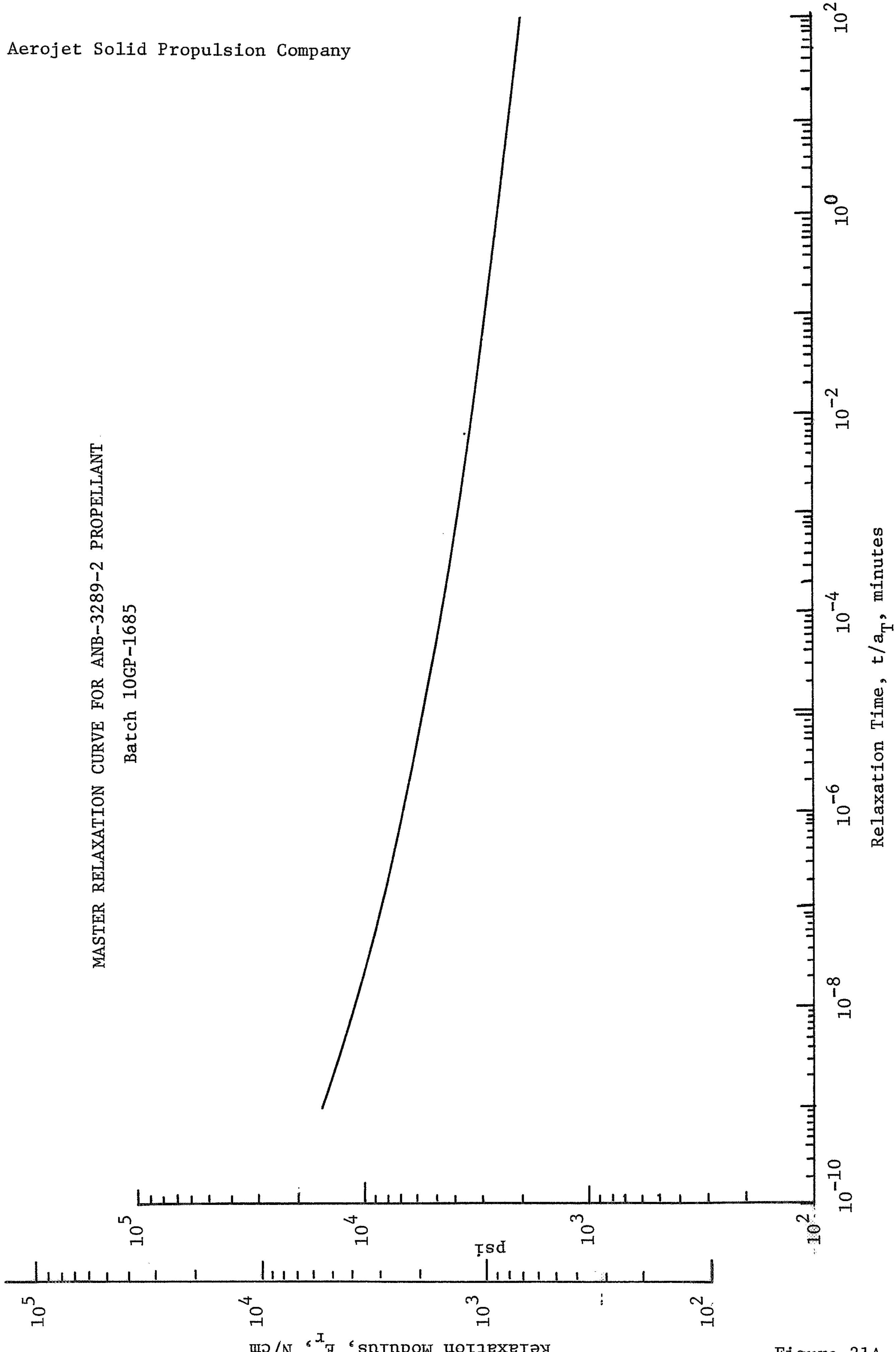


Figure 20



MASTER RELAXATION CURVE FOR ANB-3289-2 PROPELLANT
Batch 10GP-1685
Relaxation Time, t/a_T, minutes
10^{-10}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
10^{0}
10^{2}
psi
10^{5}
10^{4}
10^{3}
10^{2}
Relaxation Modulus, E_r, N/cm^2
10^{5}
10^{4}
10^{3}
10^{2}

Figure 21A

MASTER RELAXATION CURVE FOR ANB-3289-2 PROPELLANT
(Batch 10GP-1685)

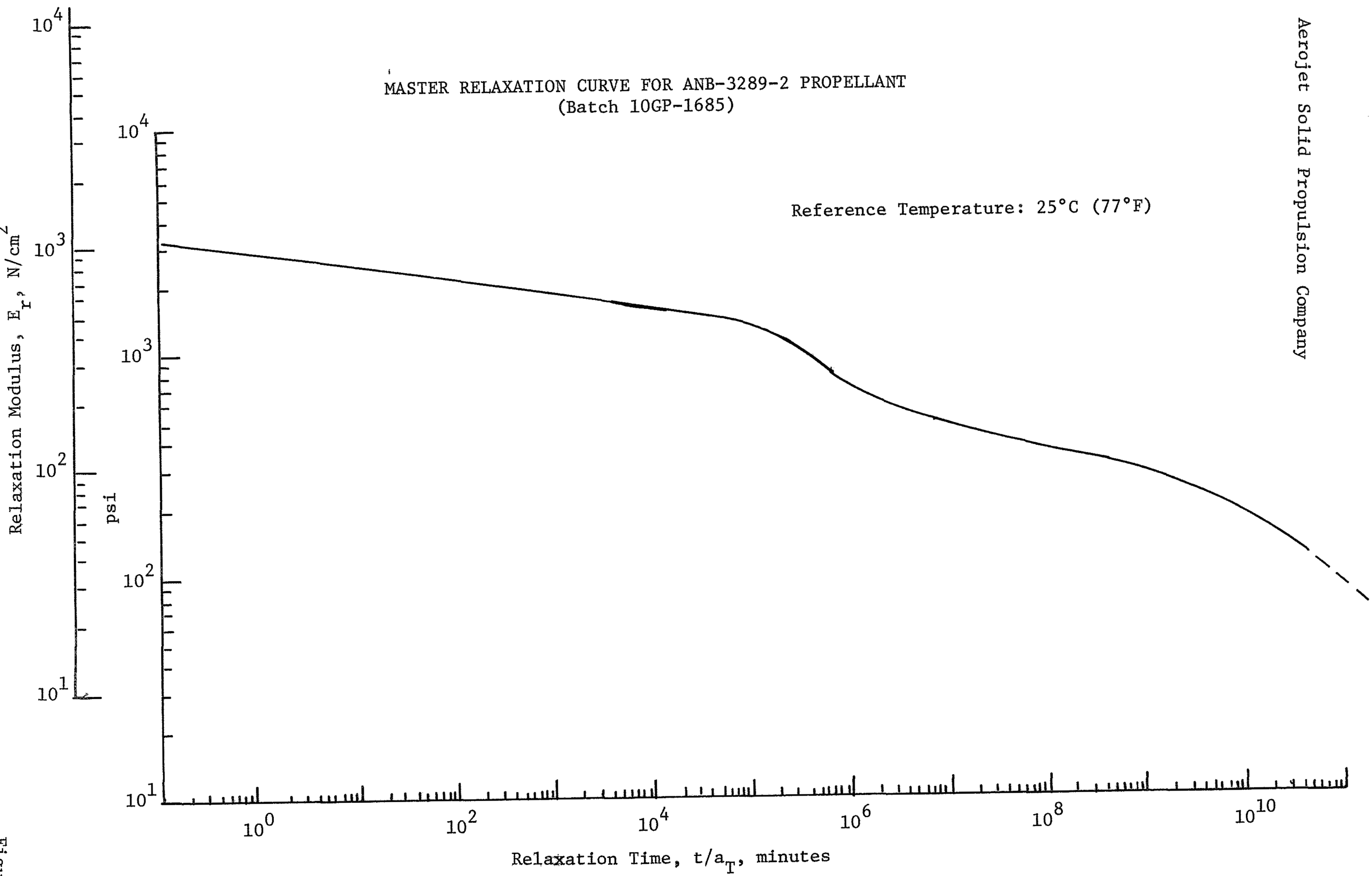


Figure 21B

TIME TEMPERATURE SHIFT FOR ANB-3289-2 PROPELLANT
(Batch 10GP-1684 and 1685)

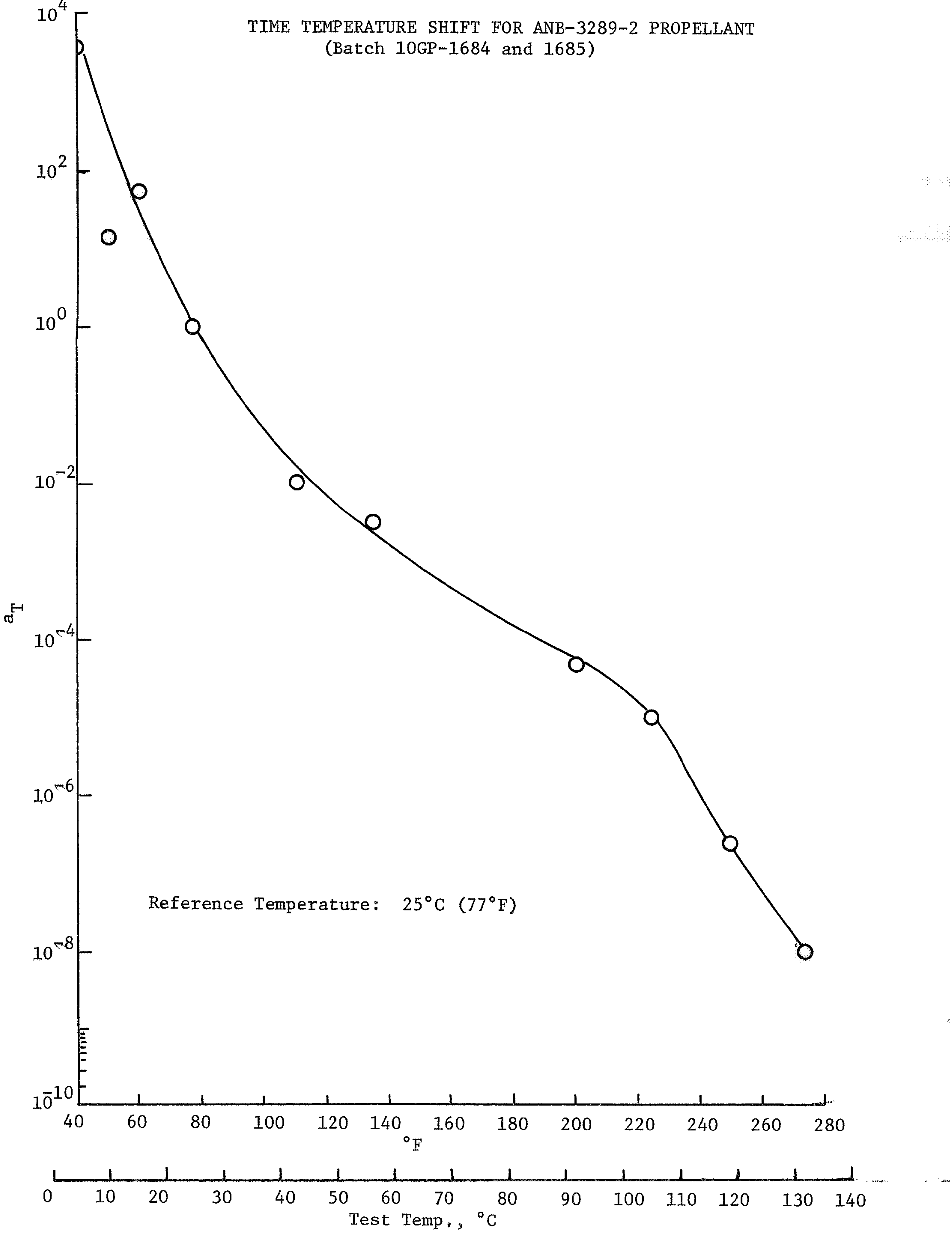


Figure 22

than anticipated relaxation modulus would indicate a lower than anticipated bond stress. The discontinuity, however, implies a change in propellant characteristics with storage at temperatures above 93°C (200°F) or in other words, a possible shift in the zero stress temperature. This shift may therefore occur even though previous tests had indicated it to be extremely small for ANB-3289-2 propellant. This change could imply that some propellant bonds either in the binder network or between binder and filler are broken under stressed conditions and reformed in a non-stressed condition because the tensile properties of ANB-3289-2 propellant have been shown to be little changed by heat sterilization as shown in Figure 5.

Bonding Properties - Constant rate shear measurements on poker chip specimens of ANB-3289-2 propellant bonded to SD-886 liner and GenGard 4030 insulation were conducted at 25, 66 and 135°C (77, 150 and 275°F) using crosshead rates of 5.08, 0.508 and 0.0508 cm/min (2.0, 0.2 and 0.02 in./min). The specimens were prepared from propellant batch No. 10GP-1684 with the crosslinker concentration of 43 equivalents required for an ambient temperature modulus of 1380 N/cm^2 (2000 psi). The shear values obtained, time to failure and the failure mode are presented in Figure 23. Unfortunately, both at 25 and 135°C (77 and 275°F) the bond failures were of a secondary type occurring in the bonds between propellant and metal plate. The true shear values are therefore higher and the values obtained represent a conservative minimum. These values are about 50% of the tensile values obtained for the tensile specimens, rather than the 70% normally obtained. Because of the limited number of specimens no further tests could be made so that these lower values were used for design considerations. A plot of the data relating bond shear strength to time to break is presented in Figure 24.

Constant rate bond tensile measurements conducted with similar poker chip specimens were made at -18, 25 and 66°C (0, 77 and 150°F) at crosshead rates of

SHEAR STRENGTH OF ANB-3289-2/SD-886/Gen Gard 4030 BOND
(Batch 10GP-1684)

Test	Test Temp. °C	Test Temp. (°F)	Crosshead Rate cm/min	Crosshead Rate (in./min.)	Stress N/cm^2	Stress (psi)	Time Min.	Mode of Failure CP(1)	Mode of Failure CPI(2)	Mode of Failure F(3)
Constant Rate Shear	25	(77)	5.08	(2.0)	101	(146)	0.048			100
					109	(158)	0.046			100
			0.508	(0.2)	74	(107)	0.220			100
					81	(117)	0.160			100
			0.0508	(0.02)	56.4	(81.8)	2.50			100
					60.6	(87.8)	3.30			100
	66	(150)	5.08	(2.0)	58.9	(85.3)	0.040		100	
					47.8	(69.3)	0.029		100	
			0.508	(0.2)	43.8	(63.5)	0.288		100	
					39.2	(56.9)	0.298		100	
	135	(275)	5.08	(2.0)	33.2	(48.1)	0.021			100
					30.6	(44.4)	0.028			100
			0.508	(0.2)	27.6	(40.0)	0.290			100
					23.9	(34.6)	0.241			100
			0.0508	(0.02)	21.5	(31.1)	3.50			100
					15.7	(22.8)	3.15			100

(1) CP - Cohesive failure in propellant
(2) CPI - Cohesive failure in propellant near bond interface
(3) F - Secondary bond failure between propellant and plate used in specimen preparation.

Figure 23

EFFECT OF BOND SHEAR STRENGTH ON TIME-TO-BREAK
ANB-3289-2 PROPELLANT
Batch 10GP-1684

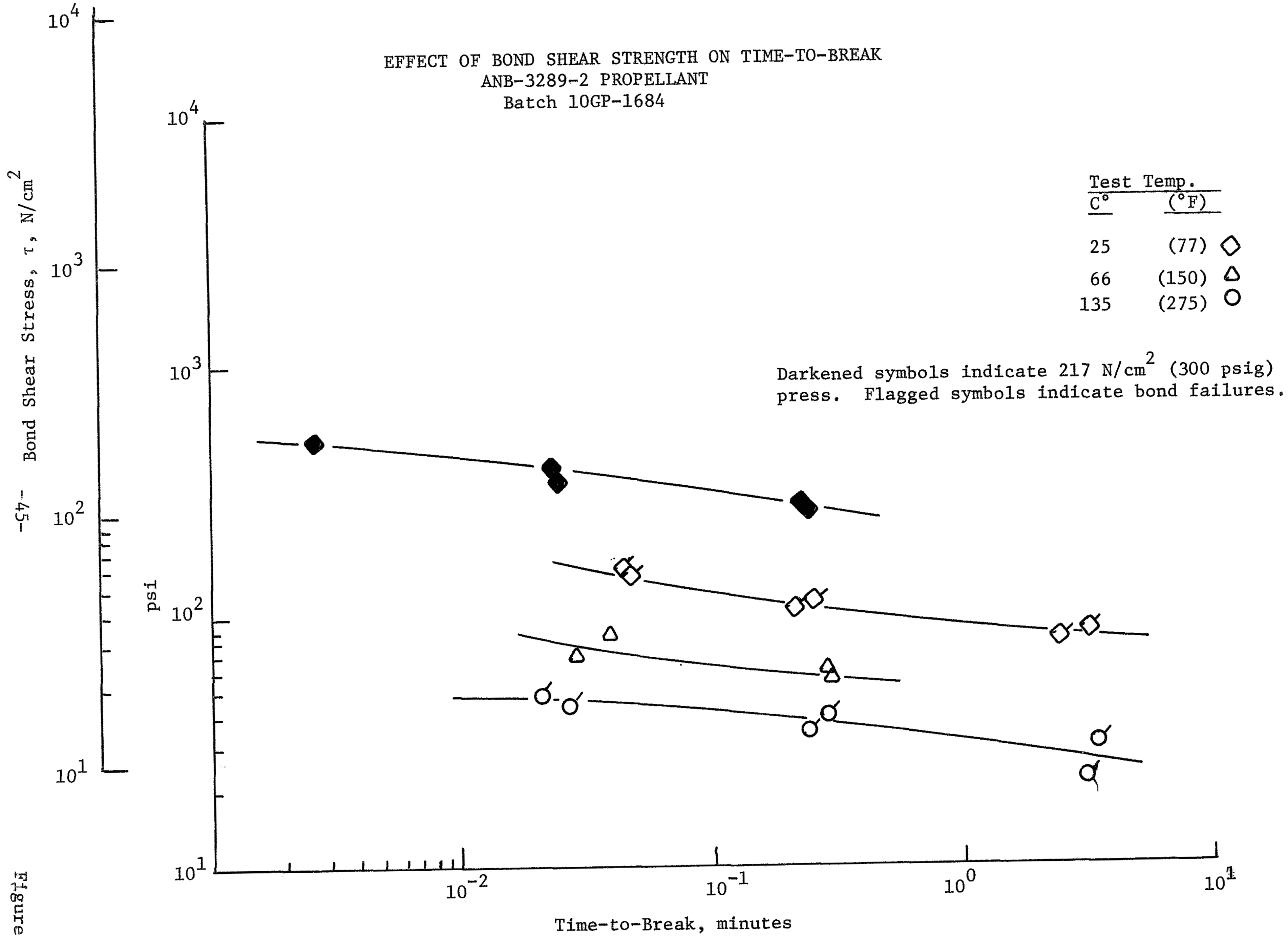


Figure 24

5.08, 0.508 and 0.0508 cm/min. (2.0, 0.2 and 0.02 in./min). The tensile values, time to failure and failure mode for each test are presented in Figure 25. Unfortunately again, some secondary bond failures occurred and these represent minimum values. As in the shear tests, no adhesive failures were observed. These data are presented in Figure 26.

High rate shear tests were also conducted at 25°C (77°F) to provide information on bond capabilities under firing conditions. A pressure of 207 N/cm^2 (300 psi) was selected as approximately that anticipated for a full-scale motor and tests performed at strain rates of 5, 50 and 500 min^{-1}. These data are presented in Figure 27. A plot of the data is shown in Figure 28.

F. PHYSICAL PROPERTIES

The thermal coefficient of expansion of ANB-3289-2 was measured by both a linear technique and by a buoyancy technique. The buoyancy technique though more commonly accepted cannot be used at temperatures over 10°C (+50°F) and hence is only applicable if no variation from linearity occurs at high temperature.

Linear measurements were made over a temperature range of 32 to 77°C (89 to 171°F) and -39 to 46°C (-38 to 115°F). The values obtained were 9.25×10^{-5} cm/cm/°C (5.14×10^{-5} in./in./°F) and 1.02×10^{-4} cm/cm/°C (5.67×10^{-5} in./in./°F), respectively. Measurement of the thermal coefficient of expansion by a buoyancy technique over a temperature range of -40 to 10°C (-40 to 50°F) resulted in a value of 1.15×10^{-4} cm/cm/°C (6.4×10^{-5} in./in./°F).

To insure that no anomalies occurred in the thermal expansion of ANB-3289-2 propellant at temperatures up to 135°C (275°F), measurements of the thermal expansion of the propellant were repeated, covering in two experiments the range 25 to 149°C (77 to 300°F) using specimens from two separate batches of propellant. No

TENSILE STRENGTH OF ANB-3289-2/SD-886/Gen Gard 4030 BOND
(Batch 10GP-1684)

Test	Test Temp., °C	(°F)	Crosshead Rate cm/min.	(in./min.)	Stress N/cm^2	(psi)	Time, min.	Mode of Failure $CP^{(1)}$	$CPI^{(2)}$	$F^{(3)}$
Constant Rate Tensile	-18	(0)	5.08	(2.0)	373	(541)	0.040			100
					517	(749)	0.046		100	
			0.508	(0.2)	452	(655)	0.500			100
					425	(616)	0.400			100
			0.0508	(0.02)	361	(523)	5.00		100	
					317	(459)	4.05			100
	25	(77)	5.08	(2.0)	191	(277)	--			100
					176	(255)	0.044	20	80	
			0.508	(0.2)	166	(240)	0.340	100		
					148	(214)	0.340	100		
			0.0508	(0.02)	99	(144)	2.90	90	10	
					123	(178)	2.60	80	20	
	66	(150)	5.08	(2.0)	105	(152)	0.047	100		
					94	(136)	0.048	80	20	
			0.508	(0.2)	51	(74)	0.290	30	70	
					70	(102)	0.338	100		
			0.0508	(0.02)	49	(71)	2.70	40	60	
					37	(54)	2.65	100		

(1) CP - Cohesive failure in propellant
(2) CPI - Cohesive failure in propellant near bond interface
(3) F - Secondary bond failure between propellant and plate used in specimen preparation

Figure 25

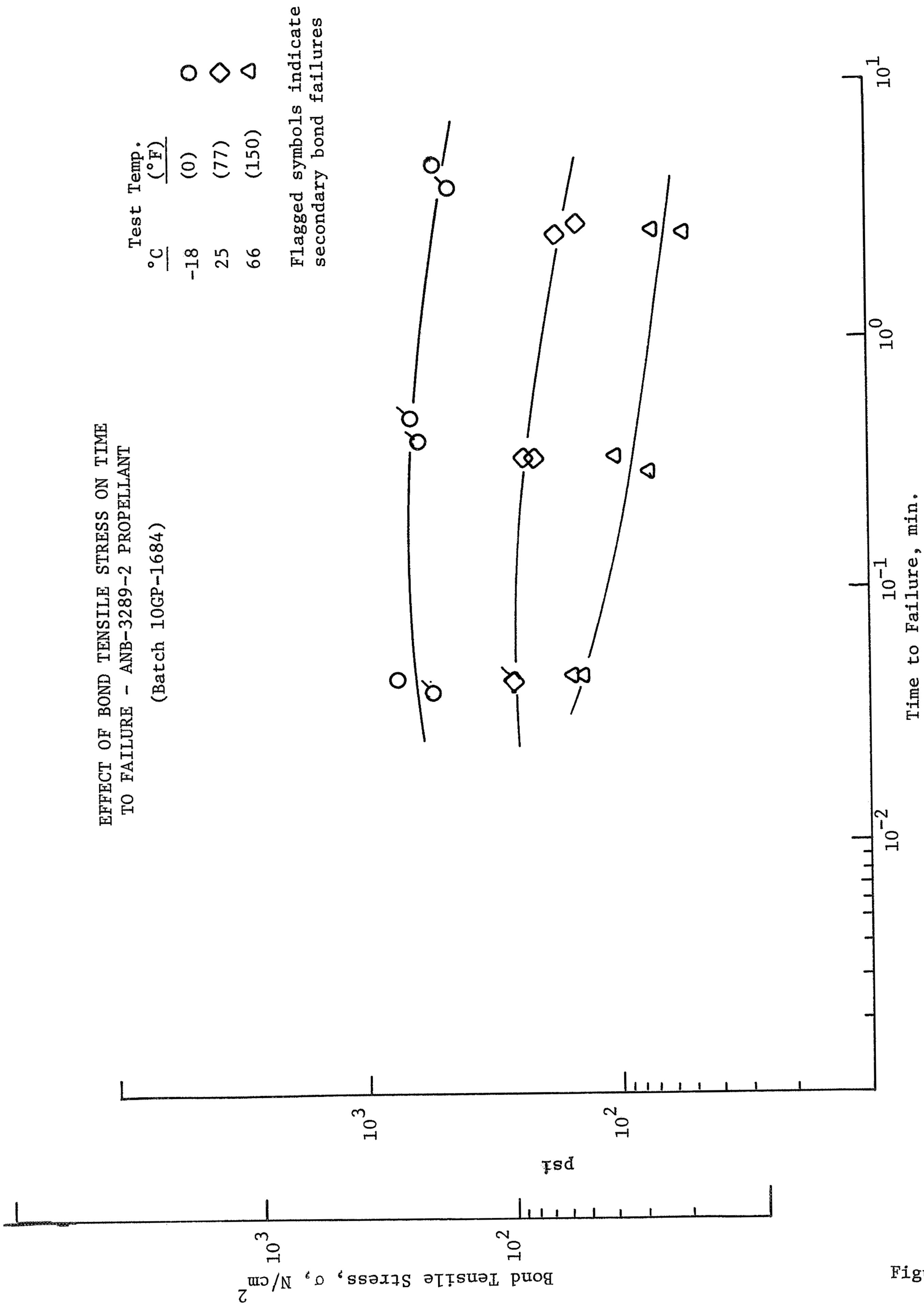

EFFECT OF BOND TENSILE STRESS ON TIME
TO FAILURE - ANB-3289-2 PROPELLANT
(Batch 10GP-1684)
Test Temp.
°C (°F)
-18 (0)
25 (77)
66 (150)
Flagged symbols indicate
secondary bond failures
10^{-2}
10^{-1}
10^{0}
10^{1}
Time to Failure, min.
10^{2}
10^{3}
psi
Bond Tensile Stress, σ, N/cm^2

Figure 26

EFFECT OF STRAIN RATE ON SHEAR STRENGTH OF ANB-3289-2/
SD-886/GenGard 4030 BOND UNDER 217 N/cm^2 (300 psig) HYDROSTATIC PRESSURE

Test	Test Temp. °C	Test Temp. (°F)	Strain Rate, min^{-1}		Stress N/cm^2	Stress (psi)	Time, Min	Mode of Failure CP[(1)]	Mode of Failure CPI[(2)]	Mode of Failure F[(3)]
High Rate Shear	25	(77)	5		194	(281)	13.87		100	
					184	(266)	15.00		100	
				$\bar{x}$	189	(274)	14.4			
			50		275	(399)	1.40		100	
					238	(345)	1.50		50	50
				$\bar{x}$	257	(372)	1.45			
			500		357	(518)	0.160		100	
					337	(489)	0.1600		100	
				$\bar{x}$	348	(504)	0.160			

(1) CP - Cohesive failure in propellant
(2) CPI- Cohesive failure in propellant near bond interface
(3) F - Secondary bond failure between propellant and plate used in specimen preparation

Figure 27

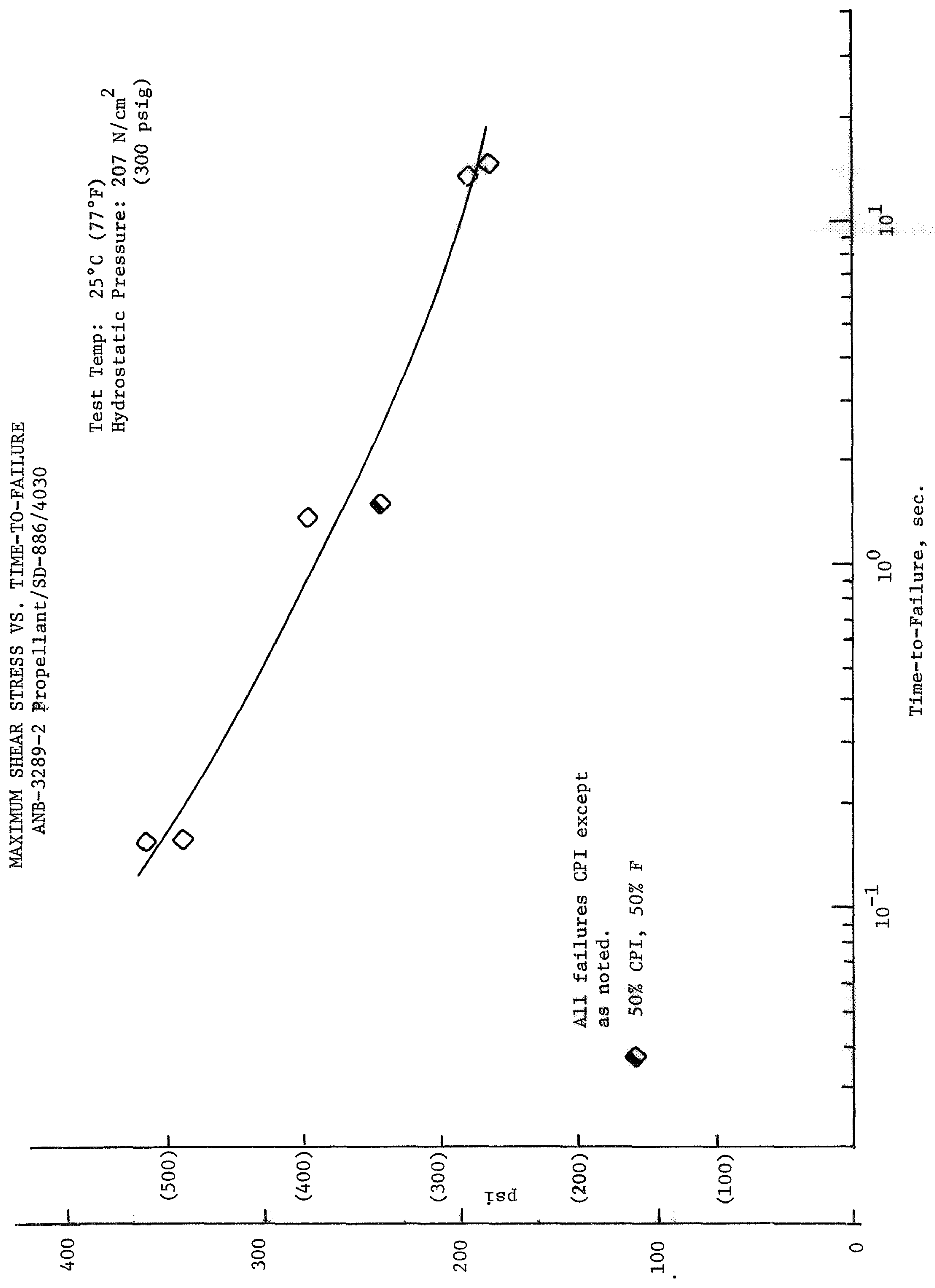

MAXIMUM SHEAR STRESS VS. TIME-TO-FAILURE
ANB-3289-2 Propellant/SD-886/4030
Test Temp: 25°C (77°F)
Hydrostatic Pressure: 207 N/cm2
(300 psig)
All failures CPI except
as noted.
50% CPI, 50% F
Time-to-Failure, sec.
10-1
100
101
psi
(100)
(200)
(300)
(400)
(500)
N/cm2
0
100
200
300
400

Figure 28

deviation from linearity was observed in either experiment and the replicate values for thermal coefficient of expansion determined were as follows:

Propellant	0°C	(°F)	Thermal Coefficient of Expansion, cm/cm/°C	(in./in./°F)
10GP-1685	25-130	(77-266)	1.05×10^{-4}	(5.84×10^{-5})
			1.04×10^{-4}	(5.77×10^{-5})
10GP-1620	25-149	(77-300)	1.06×10^{-4}	(5.89×10^{-5})
			1.01×10^{-4}	(5.62×10^{-5})

The solid density at 25°C (77°F) of ANB-3289-2 propellant was measured and found to be 1.736 g/cm^3 (0.06272 lbs/in^3).

G. HEAT STERILIZATION TESTS

All of the data collected on physical properties, mechanical properties, stress relaxation and bond integrity was used in a stress analysis to determine strain and bond tensile allowables for the propellant, insulation and bonding system. Using this analysis a strain motor grain design was generated that would insure (1) that shear stress would not be a cause of bond or propellant failure and thus cloud the interpretation of failure data, and (2) that the three strain levels selected for the test program would on projection provide for a high strain level at which failure should occur, a level at which failure would be probable, and finally a low strain level at which the chance of successful heat sterilization would be high.

In the proposed program strain levels of 3, 6 and 9% were arbitrarily selected as having a probability of meeting the above requirements. The strain motors selected for the study were 35.6 cm (14 in.) lengths of aluminum rocket motor casings. These aluminum motor cases have an inside diameter of 6.668 cm (2.625 in.) and an outside diameter of 6.985 cm (2.75 in.).

Because of scheduling problems the strain cylinders were cast using the arbitrarily selected strain levels. It was planned that stress analysis (which was lagging behind schedule) should indicate these strain levels to be too severe the bore would be machined in accordance with the findings. Nine strain cylinders and 22 double plate tensile specimens were cast from five 5000g propellant batches.

The core release previously selected and used in casting these grains was a Teflon release applied by a spray technique. This release system was selected on the basis of experience with other propellants where, in most instances, it performed well. Tests to select a core release system were not included in the demonstration program plan. The selected release was a particularly unfortunate choice for the current program because the cores are inserted through a guide into the freshly cast grain. The poor adhesion of this Teflon to the core makes it possible to scrape off portions of the release during core insertion. Subsequent tests have also revealed that the Teflon MS-122 release gives inconsistent results in releasing ANB-3289-2 propellant.

Examination of the grains showed that some propellant had adhered to the aluminum cores in longitudinal patches and had torn loose from the surface of the grains. Longitudinal cracking occurred at the edges of the torn areas where the stress would be highest on cooldown (the cores are held rigidly in place during cure and cooldown by fixed plexiglass end caps). Machining of the grains revealed that the cracks continued all the way to the liner interface. The cracks did not extend to the ends of the grain. It was concluded that cracking resulted from very high stress concentrations induced at the discontinuity produced by the bonding of propellant to the core.

Simultaneously, completion of stress analysis for the cylinders indicated that the length over diameter ratios for the strain cylinders selected were unrealistic as related to full-scale motors. The bore diameters arbitrarily selected exceeded the capabilities of the propellant liner system. Therefore the motor length and grain configuration were modified to be consistent with the recommendations of the stress analyst and a new set of motors cast using a core release found in subsequent experiments to perform satisfactorily.

The results of the stress analyses, the selected final grain design, techniques followed in insulating, lining, casting and curing the grains and finally the results of heat sterilization testing of the strain motors and bond specimens are described in the following paragraphs.

Grain Stress Analysis on the Original Grain Configuration - Completed stress analyses assuming no shift in the stress free temperature from the 57°C (135°F) cure temperature for the original grain configuration indicate that failure would occur in propellant-to-liner bond because of the high tensile stress near the center of the grain. Further, the analysis showed that only at the 3% strain level could survival be anticipated. This was the result of the high L/D selected and the unrealistic high web fraction. The web fraction required in the cycling cylinders to produce the desired strain levels significantly exceeded the web fraction of conventional full-scale motors and therefore induced a bond stress level significantly above that anticipated in a full-scale motor design. For example, the 1000 min. bond stress for the smallest bore was calculated to be $62N/cm^2$ (90 psi) with a propellant/liner bond allowable of only $24N/cm^2$ (35 psi). *

This calculation assumed a stress free temperature of 57°C (135°F) (cure temperature) and that no change in stress free temperature would occur. Although it was expected from the work done to date on this highly stable propellant and bonding system that the shift would be small, (a few degrees/cycle) the assumption of no shift was unrealistic. It was considered safer to assume a relatively large shift in stress free temperature to insure a margin of safety and thus provide a reasonably conservative design.

* Grain dimensions length 33 cm. (13 in), bore diameter 1.377 cm (0.542 in), grain end configuration 30° taper measured from longitudinal axis.

Motor and Grain Design Changes - To provide a more realistic length-to-diameter ratio the length of the strain cylinders was reduced by 50%. This change provided a strain cylinder with a propellant grain 15.25 cm (6 inches) in length rather than 33 cm (13 inches) as previously cast, reducing the l/d ratio from 4.7 to 2.17.

Stress analysis of the shortened motor assuming a shift in stress free temperature during heat sterilization from the 57°C (135°F) cure temperature to a value of 93°C (200°F) indicated that a more realistic selection of strain levels would be 2, 4, and 6% strain values.

A 30° taper measured from the longitudinal axis of the motor is recommended for the grain end configuration to duplicate the low shear stress of the full-scale motor. The shear stress calculated for the 4% strain level is 0.94 N/cm^2 (1.36 psi) at 135°C (275°F).

The required bore diameters to achieve these strain levels, as well as the anticipated tensile bond stresses for a time of 10 hrs and 6 months at ambient after completion of heat sterilization, are shown in Figure 29. The initial strains anticipated for these bore diameters are shown for comparison purposes. Propellant allowables are included to indicate the predicted margins of safety and possible failure modes. These selected strain levels provided a series of motors in which failure would be anticipated for the highest strain level, the middle strain level should be marginal and the lowest level should provide a fairly large margin of safety. The calculations showed that if no shift in stress free temperature occurs, all strain levels would survive. There should be no difficulty in providing a full-scale motor grain design compatible with the lowest strain level included in the test program.

EFFECT OF BORE DIAMETER ON
PREDICTED LIFE OF STRAIN CYLINDERS

	Calculated Stresses and Strains (1)			Propellant Capability	
Bore Diameter, cm	4.034	2.662	1.986	Relaxation Modulus N/cm^2 (psi)	Propellant Allowables
Initial Strains at 25°C (77°F)/%	0.99	1.97	2.96		
Maximum Strain,(2) %					
Sterilization +10 hrs. at 25°C (77°F) storage	2.09(3)	4.18(4)	6.27(3)	1311 (1900)	7.0
Sterilization +6 months at 25°C (77°F) storage	∿2.09	∿4.18	∿6.27	759 (1100)	7.0
Bond Stress, N/cm^2					
Sterilization +10 hrs. at 25°C (77°F)	12.6 (18.3 psi)(3)	30.2 (43.7 psi)(4)	47.6 (69.0 psi)(3)	1311 (1900)	(44.0 psi)
Sterilization +6 mos. at 25°C (77°F)	7.3 (10.6 psi)(3)	17.5 (25.4 psi)(4)	27.6 (40.0 psi)(3)	759 (1100)	(24.0 psi)

(1) Assumed stress free temperature 93°C (200°F)
(2) At motor midpoint.
(3) Ratioed from calculated value at 4% strain.
(4) Calculated value.

Figure 29

Strain Cylinder Insulation and Lining - Nine, one-half length 7 cm (2.75 in) diameter motor cases were sandblasted and then coated internally with FM-47 metal primer. They were then insulated with 1.52 mm (60 mil) GenGard V-4030 insulation (unvulcanized) using Chemlok 220 adhesive. Cure and vulcanization was conducted at 149°C (300°F) using vacuum bagging and an autoclave pressure of 103.5 N/cm^2 (150 psi). The insulation flowed sufficiently during the bonding process to essentially eliminate the seam line. The insulated cylinders were trimmed at each end to fit the propellant casting tooling and the interior surface sanded, and baked 24 hr. at 149°C (300°F).

After the first motor lining and casting and unsuccessful core stripping the propellant and liner was removed from five of the motors leaving only the insulation. These motors were cut in two to provide 10, 17.8 cm (7 in.) motors.

Nine of the motors were set aside for the casting of case bonded strain motors. The insulation in the tenth motor was modified to provide a stress relieved design back-up system. The insulation in this cylinder was laid up in three layers. The outer layer (the original insulation) was bonded to the motor case with Chemlok 220 adhesive. The middle insulation layer was strip bonded to both the outer and inner insulation layers in alternating bands as shown in Figure 30. The layed up was sanded, cleaned and then given the same 149°C (300°F) heat treatment used with the stress designed cylinders to insure removal of all migratory species.

All ten cylinders within 72 hrs. of propellant cast were lined with SD-886 liner, the liner cured for 48 hrs. at 43°C (110°F) and then baked at 149°C (300°F) for 12-24 hrs. to remove all catalyst and any volatile components.

END VIEW STRESS RELIEVED MOTOR

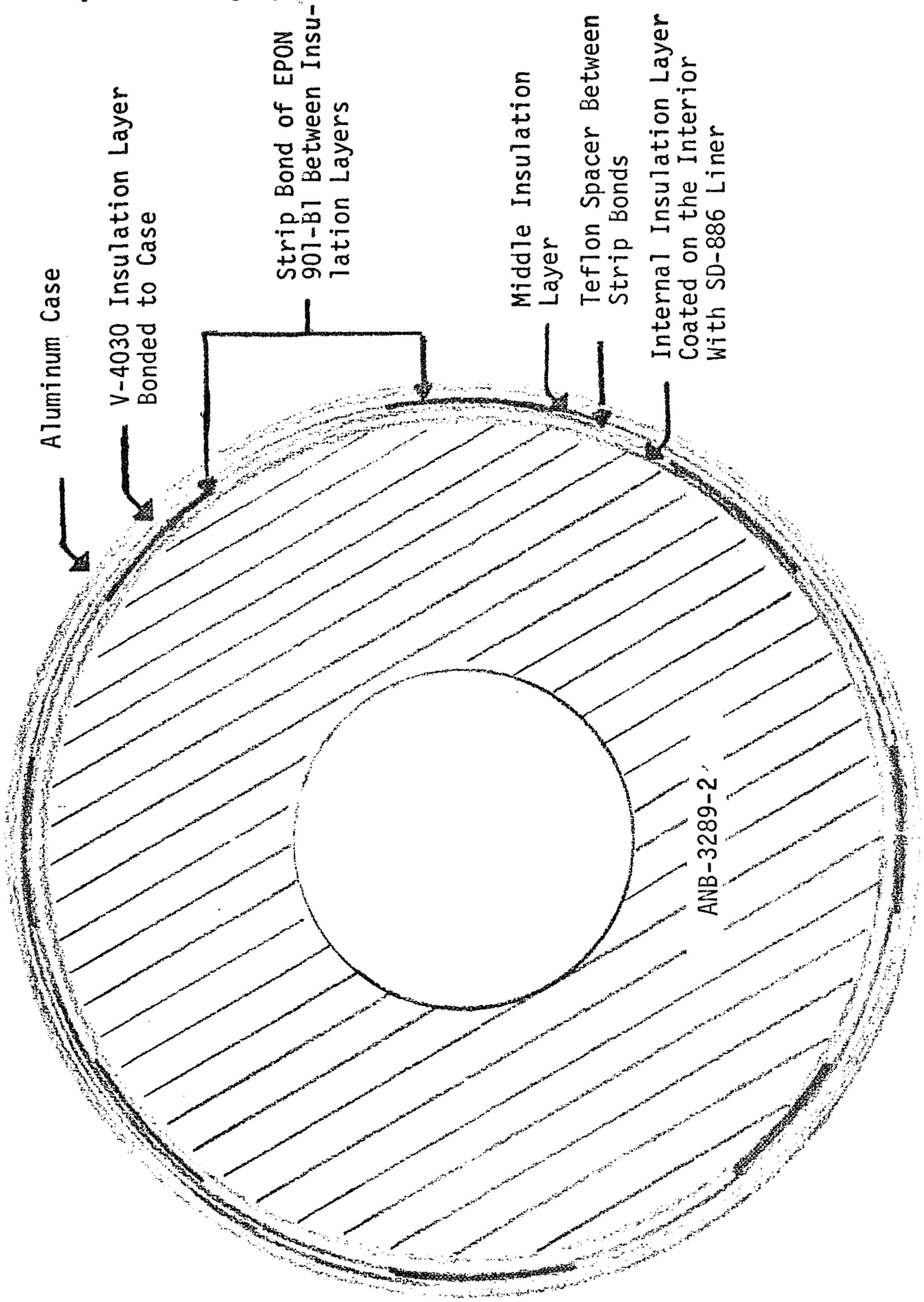


Figure 30

Propellant Cast and Cure - The ten strain motors were cast from two 4.54kg (10 lb) batches of ANB-3289-2 propellant adjusted to a modulus of 1380 N/cm^2 (2000 psi) (43 equivalents of trimethylopropane). The propellant was mixed and cast at 63 to 66°C (145 to 150°F) to ensure good flow characteristics. The program required purification of additional Telagen-S polymer in order to provide sufficient propellant for the motor casting.

The casting technique employed was designed to prevent any folding of propellant to entrain air. The cylinders were bottom cast from the mixing pot using a diaphragm to displace the propellant with vacuum on the motor to draw the propellant into the motor and to degass the liner surface. A diagram of the casting assembly is shown in Figure 31. Propellant was drawn up into the vacuum bell to remove any surface bubbles from the motor and the aluminum core inserted immediately after breaking vacuum. Most of the cylinders were cast with essentially no collapse on breaking vacuum, indicating little air entrapment. In a few instances, however, gas leaks at the face of the cylinders caused some air to rise through the propellant. The very low viscosity of the propellant at the 66°C (150°F) casting temperature, it is believed, aided degassing in these cases.

To insure that the cores released properly, Q-92, a baked-on, tough polymeric silicone release agent which has been found to release satisfactorily from ANB-3289-2 propellant was used. As additional insurance of release the Q-92 coated cores were wiped with DC-11 silicone release just prior to insertion. This treatment has been beneficial. To eliminate the danger of scraping off any of the release agent the opening in the cover plate was enlarged and chamfered so that no abrading of the release agent could occur.

STRAIN MOTOR CASTING ASSEMBLY

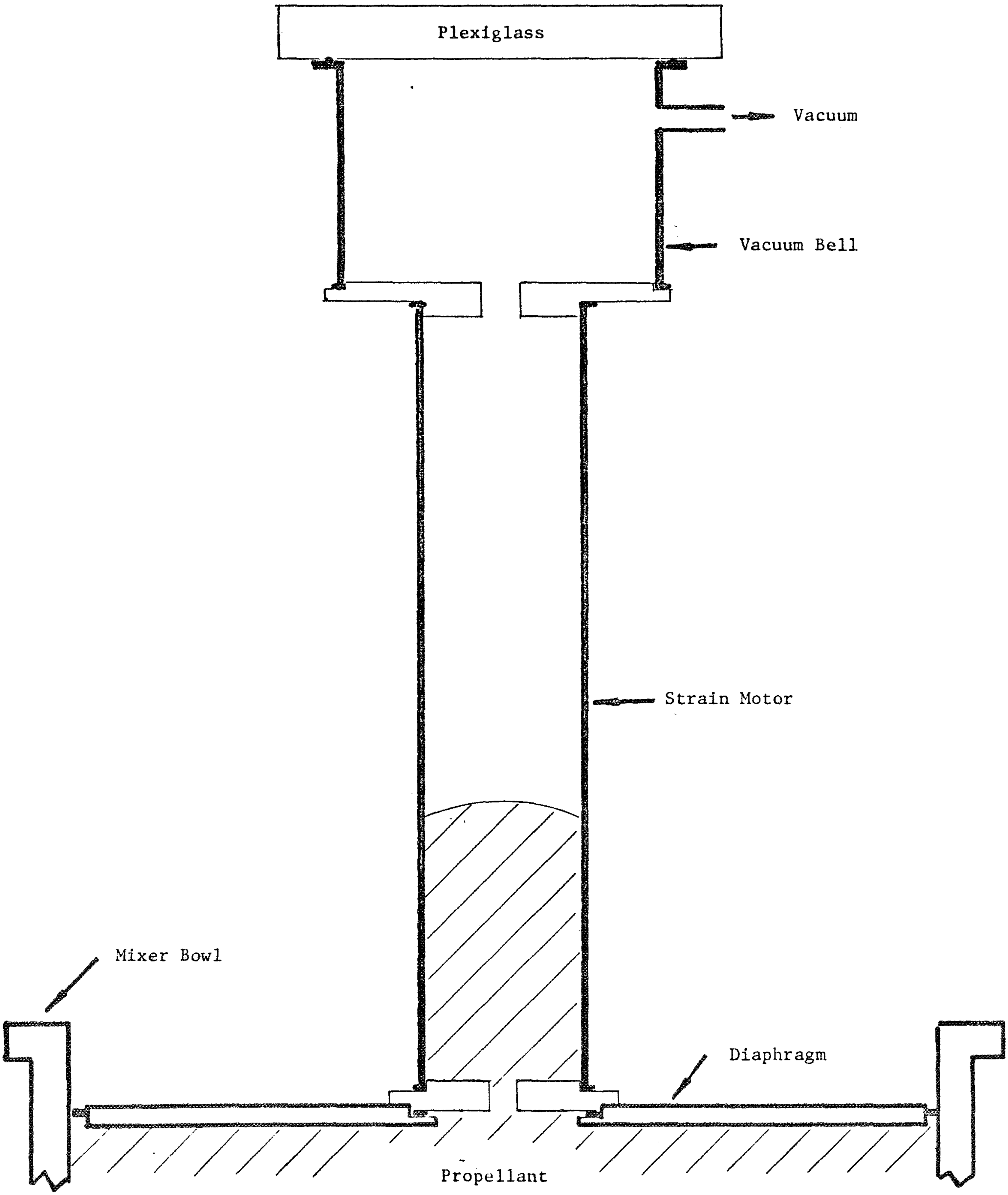


Figure 31

The cast grains were cured at 57°C (135°F) for 2 weeks and after cure machined to the final end configuration and to the proper bore diameter and end configuration.

Strain Cylinder Sterilization - Thermal diffusivity data indicate that a 55 hr soak at 135°C (275°F) is adequate to insure, for the motor sizes involved, a minimum of 53 hrs at sterilization temperature. The heat-up and cool-down program for each heat sterilization cycle was selected in an attempt to minimize transient bond stresses. The heat-up program was as follows:

1. The grains after measurement and tap testing at 25°C (77°F) were placed in an air circulated 57°C (135°F) oven and allowed to soak for 18 hours.

2. After this equilibration the strain motors were then transferred to the 135°C (275°F) air circulated oven for heat sterilization.

This program was selected because the motor case heats more rapidly than the propellant. Expansion of the case away from the grain increases the bond stress and by initially heating to 57°C (135°F) (the initial stress free temperature) this increased stress is imposed under temperature conditions at which the propellant and bond strengths remain reasonably high. Final heat-up, 57-135°C (135-275°F) is then conducted under conditions where the grain should be under compression.

The cool-down procedure followed was to shut off the 135°C (275°F) oven and allow the oven and contents to cool to about 107°C (225°F) (approximately one hour required) and then transfer the grains directly to the 25°C (77°F) air circulated oven for equilibration prior to bore measurement. Rapid cool-down would tend to keep the grains under compression during the bulk of the temperature drop and minimize bond stresses.

A plot of the temperature time history experienced by the motors is shown in Figure 32. Results of X-ray exmaination of the nine stressed motors indicated the liner to be somewhat uneven and the presence of low density areas in the liner. These low density areas may represent foamy or void containing liner. This is not uncommon in SD-886 liner. The propellant grains were also found to contain a few voids. The void count for the various motors were as follows:

Motor No.	Propellant Voids
1	6 to 0.32 cm
2	1 - 0.56 cm
3	2 to 0.46 cm
4	3 to 0.32 cm
5	7 to 0.83 cm
6	6 to 0.32 cm
7	3 to 1.27 cm
8	4 to 0.70 cm
9	1 - 0.89 cm

As expected the cylinder prepared with the stress relieved insulation after the first cycle measured no strain after six heat cycles as shown in Figure 33. Radiographic examination of this grain after three and six cycles showed the insulation propellant bond line to be free of any separations and the propellant to be in excellent condition. The grain itself on visual examination appeared unchanged by the sterilization treatment.

STRAIN MOTOR HISTORY - HEAT STERILIZATION

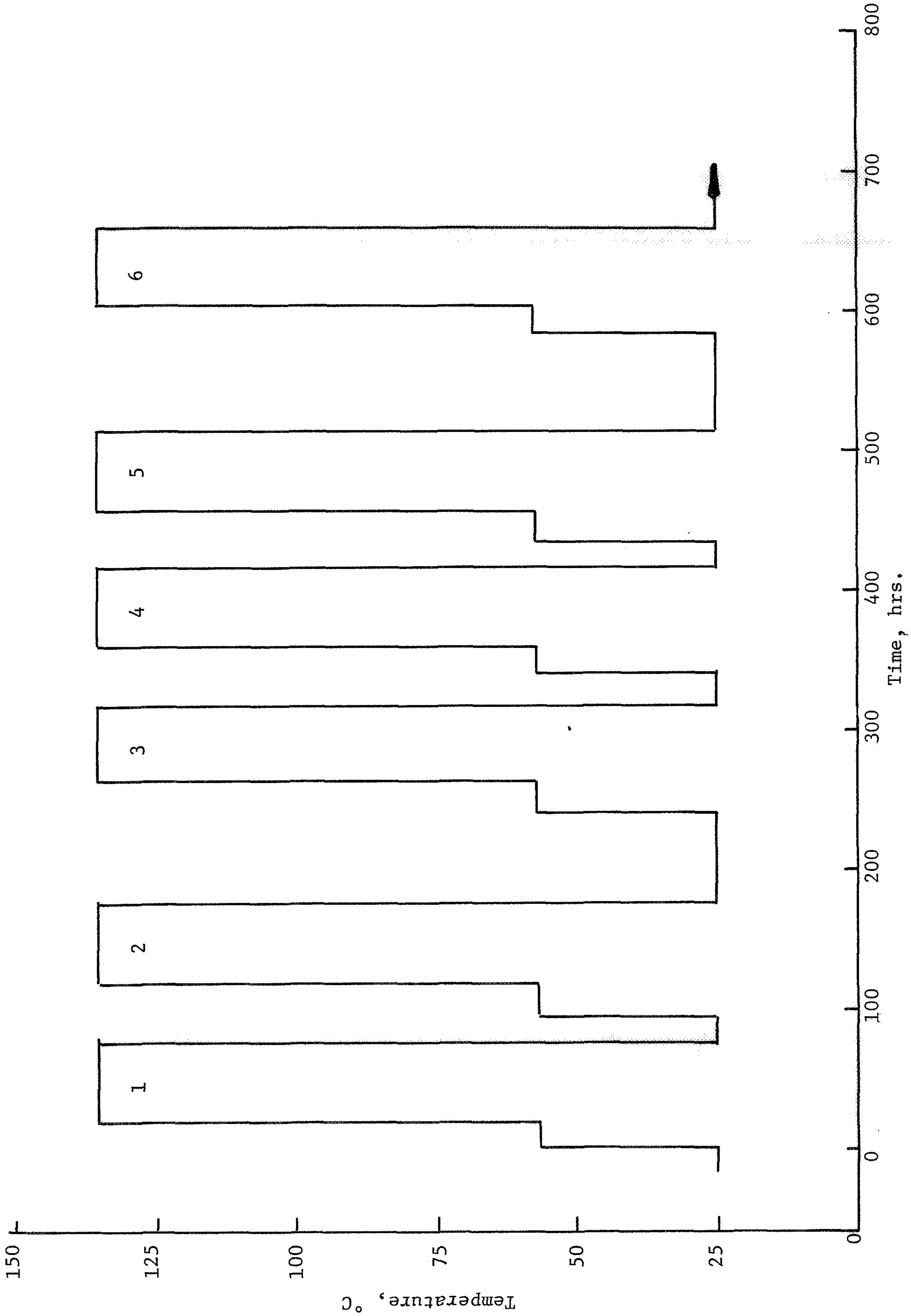


Figure 32

EFFECT OF HEAT STERILIZATION ON THE
INTEGRITY OF 7 cm (2.75 in) DIAMETER STRAIN MOTORS

(ANB-3289-2 Propellant/SD-886 Liner/Gen Gard V-4030 Insulation)

Motor	Initial Bore Diameter		Anticipated Strain		Calculated Strain at 25°C (77°F), %						
No.	cm	(in.)	Initial	After Sterilization	Initial	1 Cycle	2 Cycles	3 Cycles	4 Cycles	5 Cycles	6 Cycles
1	1.986	(0.782)	2.96	6.27	2.9	1.4	F(2)	--	--	--	--
2	1.986	(0.782)	2.96	6.27	3.7	F(2)	--	--	--	--	--
3	1.986	(0.782)	2.96	6.27	3.6	2.0	F(2)	--	--	--	--
7	2.662	(1.048)	1.97	4.18	1.7	1.3	F(2)	--	--	--	--
8	2.662	(1.048)	1.97	4.18	1.5	1.0	0.9	F(2)	--	--	--
9	2.662	(1.048)	1.97	4.18	1.7	1.4	1.6	F(2)	--	--	--
4	4.034	(1.588)	0.99	0.99	1.3	1.4	1.8	1.8	1.7	F(2)	--
5	4.034	(1.588)	0.99	0.99	0.9	1.1	F(2)(3)	--	--	--	--
6	4.034	(1.588)	0.99	0.99	0.9	0.9	1.0	1.1	1.0	0.9	1.0
10	2.662	(1.048)	0	0	0.3	-0.1	-0.1	-0.3	-0.6	-0.6	-0.6

(1) Strain level anticipated after 6 heat sterilization cycles if an accompanying shift in stress free temperature to 93°C (200°F) occurs.
(2) Failed by cracking longitudinally along bore.
(3) Very small crack initiating at a void in the surface near one end of the bore.

Figure 33

The case bonded stressed grains show a considerable variation in the initial strain calculated from bore measurements, and assuming an initial stress-free temperature of 57°C (135°F) this variation probably reflects variations in thickness of the hand trowelled liner. Motors numbered 1, 2 and 3, representing the highest strain level, failed early in the sterilization program. In fact, the drop off in calculated strain probably indicated initiation of some microscopic fracture. Similar, though less severe change is apparent in grains numbered 7 and 8 which developed visual cracks at the inner bore surface after 2 and 3 heating cylces, respectively.

Of the grains prepared with the lowest strain level this drop in calculated strain did not occur and one grain (#6) remained in excellent condition after the full six heat sterilization cycles as indicated by visual and X-ray examination. A second grain (#4) survived five heat cycles before developing a crack in the inner bore surface at the midpoint. The third of these grains showed a small crack initiating at a bore imperfection (a large void at the bore surface near one end) after two cycles as shown in Figure 34. This grain (#5) was bisected longitudinally in order to examine the propellant/liner/insulation interface after an additional cycle. The bond line was shown to be in excellent condition and the propellant and liner showed no evidence of any change in physical properties.

All failures occurred in strain, occurring as longitudinal cracks at the bore, there was no indication of any failure in bond tensile. This finding is particularly significant because improvements in strain capability can be achieved by a slight lowering in the total solids of the propellant and/or by reducing the modulus to a value closer to the 1173 N/cm^2 (1700 psi) previously found to be adequate in preventing the development of propellant porosity.

PHOTOGRAPH OF STRAIN MOTOR BISECTED AFTER THREE HEAT STERILIZATION CYCLES

(Surface void which initiated failure in strain visible in upper left hand corner)

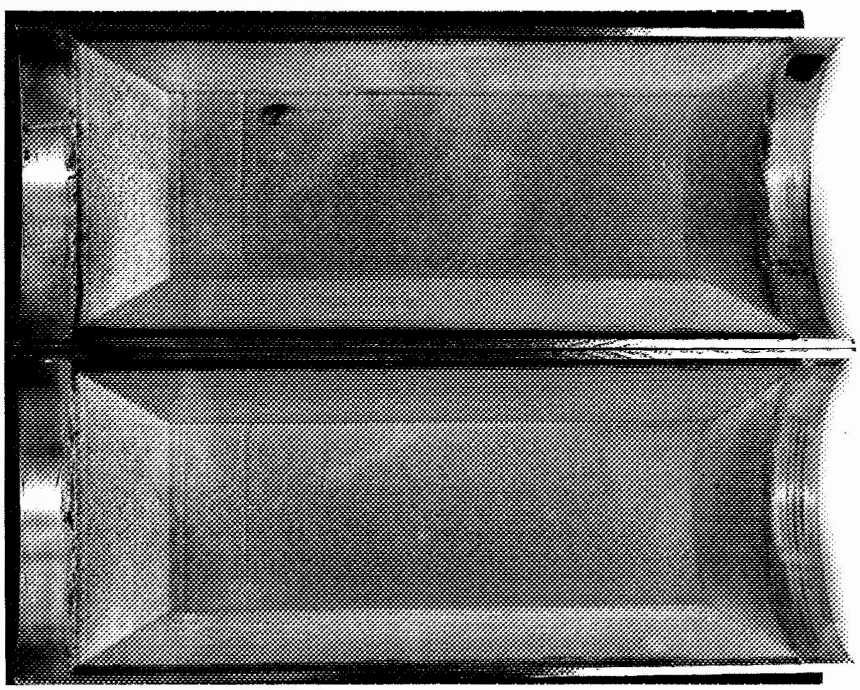


Figure 34

It is interesting to note that the anticipated changes in bore diameter which would reflect an increase in calculated strain with successive heat sterilization cycles did not occur. This does not mean that significant changes in strain did not occur. The motor failures which occurred can not be attributed to severe degradation in propellant mechanical properties as it has already been shown that ANB-3289-2 propellant undergoes little change in tensile properties with heat sterilization (Figure 5).

Mechanisms which could offset a change in bore diameter are internal fracturing and or gassing of the propellant. Again preliminary studies reported in Appendix A and the visual examination of bisected sterilized grains and X-ray examination of the surviving motors show that at the selected crosslink density, porosity does not develop. The only conclusion that remains is that significant changes in stress free temperature did occur and that bore measurements alone, using a conventional stress analysis, are inadequate to detect these changes. That this is possible is apparent if one considers the actual changes which occur during a shift in stress free temperature

The significance of stress-free temperature changes is best seen in some simple considerations of an infinitely long cylindrical grain (where there are no end-effects). The grain is fully case-bonded and subjected to cooling to some temperature T. The inner-bore hoop strain, ε_θ, is simply related to the stress-free temperature T_{sf}, and to T by the following relation

$$\varepsilon_\theta = K\ (T_{sf} - T) \qquad (1)$$

where K is a collection of constant terms, including those for geometry, Poisson's ratio and the coefficient of thermal expansion.

The stress-free temperature will change with changes in the chemical crosslinking in the propellant binder. Thus changes in ε_θ will occur as defined in Equation (1).

However, simple observations of the grain do not show those strain changes which are actually occurring. To understand this consider some dimensional measurements of the bore diameter which is related to ε_θ by the following:

$$\varepsilon_\theta \approx \frac{D - D_{sf}}{D_{sf}} \qquad (2)$$

where D is the bore diameter at the temperature T.

D_{sf} is the bore diameter at T_{sf}.

An evaluation of Equation (2) shows that D_{sf} must be known before ε_θ can be calculated. But D_{sf} must be measured at T_{sf}, which requires a separate evaluation. To illustrate this consider the bore diameter, D, to equal 5.08 cm (2 in.) at 25°C (77°F). At the cure temperature of the propellant, assumed to be the initial value of T_{sf}, D_{sf} = 4.93 cm (1.94 in.). This gives

$$\varepsilon_\theta = \frac{5.08 - 4.93}{4.93} = 0.031$$

After sterilization of the propellant at high temperatures, we will assume the stress-free temperature to have increased to 93°C (200°F) where we measure D_{sf} to be 4.78 cm (1.88 in.). Thus, ε_θ becomes

$$\varepsilon_\theta = \frac{5.08 - 4.78}{4.78} = 0.064$$

These two calculations show that ε_θ may differ by a large factor (greater than 2 in this instance) while the observed bore diameter, D, remains unchanged.

The evaluation of changes in T_{sf} requires stress measurement as described in Appendix B.

Measurements of the bond tensile and shear strengths of the double plate tensile specimens stored with the grains are presented in Figure 35. Although some difficulty occurred in specimen preparation (many of the DPT's exhibited poor bonds between insulation and the metal plates used in specimen preparation) the bond values reflect the same excellent bond strength and bond stability previously exhibited by the insulation/liner/propellant system.

Details of the equipment used in the heat sterilization tests as well as the actual bore measurement locations are presented in Appendix C.

EFFECT OF HEAT STERILIZATION ON THE TENSILE AND
SHEAR STRENGTH OF THE ANB-3289-2 PROPELLANT/SD-886 LINER BOND

No. of Heat Sterilization Cycles(1)	Tensile Strength			Shear Strength		
	N/cm^2	(psi)	Failure Mode(2)	N/cm^2	(psi)	Failure Mode(2)
0	52(3)	(75)	F	59(4)	(86)	F
1	86(3)	(125)	CPI	68(4)	(99)	CPI
2	72(5)	(104)	CPI	68(4)	(99)	CPI
3	88(3)	(127)	CPI	68(4)	(99)	CPI
4	117(5)	(169)	CP	58(4)	(84)	F
5	92(3)	(133)	CP	61(4)	(89)	CPI
6	104(5)	(150)	CP	61(3)	(89)	CPI

(1) 55 hr. heat soak at 135°C (275°F)
(2) Failure Mode CP - Cohesive failure in propellant
CPI - Cohesive failure in propellant near bond interface
F - Secondary failure between insulation and plate used in specimen preparation.
(3) Average of two specimens.
(4) Single specimen.
(5) Single specimen, duplicate value discarded because specimen failed due to failure between insulation and plate used in specimen preparation.

Figure 35

CONCLUSIONS

The following conclusions are drawn from the results of the heat sterilization tests.

A. The feasibility of thermally sterilizing solid rocket motors has been conclusively demonstrated by the successful heat sterilization of both a low strain, case bonded motor and a stress relieved grain design. The excellent condition of the individual components, propellant, liner, insulation, and the interfaces between these components attests to their excellent thermal stability and freedom from degradative interaction.

These results prove the validity of the approach taken in the development and selection of these components and confirm the importance of minimum chemical interaction between components during heat sterilization. Specifically, the results confirm the hypothesis that the critical factors necessary for successful heat sterilization are,

1. Stabilization of the oxidizer.

2. Selection of a thermally and oxidatively stable binder with a high crosslink density, free of migratory species or catalysts that can contribute to degradation at component interfaces.

3. Selection of a thermally stable liner with good high temperature properties, free of migratory species and catalysts which can contribute to degradation at bond interfaces.

4. Selection of a thermally and oxidatively stable insulation free of reactive migratory species.

5. Selection of processing techniques that minimize casting defect sites.

These tests indicate that a case bonded motor using the insulation liner and propellant selected and experiencing an initial maximum strain of one percent will survive heat sterilization. This survival is predicated, of course, on a heat cycle which will not induce transient strains greater than those experienced in the demonstration program. The importance of this last statement, particularly as it applies to larger motors with greater web thicknesses, will be discussed in the next section of the report (Recommendations).

B. Contrary to predictions made from equilibrium stress calculations, all failures occurred in strain rather than bond stress as indicated by longitudinal cracks initiating at the inner bore surface. The contribution of propellant casting voids to failure is quite apparent. In fact, a void located at the surface near the fore end of the grain (an area of lower strain than the midpoint) created a severe local stress gradient in grain No. 5 (a low-strain case-bonded grain) causing premature failure in this motor.

The inability to predict the failure mode from equilibrium stress analyses and the higher than predicted incidence of failures indicates the need for a more sophisticated analytical treatment. Such an analysis could include a determination of the least damaging heat-up and cool-down program. It is reasonable to believe that the heating and cooling schedule followed in the motor demonstration was unduly severe.

C. The excellent condition of the strain motor having the stress relieving insulation configuration after heat sterilization emphasizes the attractiveness of using a design of this type in full-scale motors. Again, the excellent condition of the components and bond interfaces was a prerequisite to grain and bond integrity.

RECOMMENDATIONS

Although the completed program demonstrates the feasibility of sterilizing rocket motors, by demonstrating the compatibility of all the components to heat sterilization under conditions of imposed stress and strain, the small-scale of the strain motors makes it imperative that these results be confirmed on a more realistic scale. This demonstration should be conducted in operational scale motors with realistic web thicknesses and practical grain designs culminating in confirmation of success in motor firings. The grain design for these demonstration motors should be selected on the basis of a more sophisticated stress analysis than that employed in the subscale tests. It would be particularly desirable to test both conventional case bonded and stress relieved designs.

Two conclusions drawn from the subscale demonstration are of particular importance when considering scale-up to larger webs. The first of these is the inability of the stress analysis used to adequately predict the failure mode and the implication that high transient strains induced during heat up and cool down were responsible for the higher incidence of strain failure than predicted. The increase in web thickness on scale-up and the more severe stress gradients which would thus be imposed would magnify the transient strain problem. Thus, the stress analysis must also be addressed to the selection of the least damaging heating and cooling schedule to minimize this effect. The fact that the strain capability of the propellant rather than bond strength to the insulation was the limiting factor would suggest a change in propellant solids loading in order to provide greater strain capability.

Another important factor in improving the strain capability in full-scale motors is to eliminate defect sites. The high incidence of casting voids in the subscale strain motors contributed significantly to the incidence of failure.

Preliminary processing studies to insure that such defects are minimized should be an important part of the scale-up program.

If these recommendations are followed and the grain design is limited to a very low strain requirement, a successful scale-up will be insured.

To provide a low strain design many special techniques can be considered including the use of taper, boots, spot or strip bonding or a stress relieved insulation system such as the one used in the subscale tests. In addition, techniques such as pressure curing can be considered which when used with the proper case materials lowers the stress-free temperature. All of these techniques should be considered during the design phase of the scale-up study.

GLOSSARY OF TERMS AND SYMBOLS

Chemlok 220	A rubber to metal adhesive manufactured by Hughson Chemical Company
Chemlok 203	A metal primer for use with Chemlok 220
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DARCO S-51RL	An activated carbon black manufactured by Atlas Chemical Industries
DC-11	A silicone grease manufactured by Dow Corning
Dimeryl Diisocyanate	A hindered isocyanate curing agent manufactured by Quaker Oats Company
DPT	Double plate tensile specimens, rectangular in cross section
DTA	Differential thermal analysis
FM-47	Vinyl phenolic structural adhesive
GenGard V-45	A nitrile butyl rubber insulation manufactured by General Tire Company
GenGard V-4030	An ethylene propylene rubber insulation manufactured by General Tire Company
HSMP	High speed Mikropulverizer grind oxidizer, average particle size 30μ
I_s	Specific Impulse
Q-92	Silicone release manufacturing by Dow Corning
SD-850 Insulation	A castable, trowelable insulation manufactured by Aerojet Solid Propulsion Company
Telagen-S	Secondary hydroxyl terminated saturated polybutadiene polymer manufactured by General Tire Company.
TMP	Trimethylolpropane

GLOSSARY OF TERMS AND SYMBOLS (cont.)

σ_m	Maximum stress
σ_f	Stress at failure
ε_m	Strain at maximum stress
ε_f	Strain at failure
E_o	Instantaneous modulus

APPENDIX A

Oxidizer Stability - The instability of standard as-received ammonium perchlorate at high temperature has been well established.[3] A great deal of experimental work has been done with AP yet no single theory of AP decomposition has been developed which is acceptable to all workers in the field. Part of the reason for this is the complexity which results from the fact that the material decomposes by two different paths both of which are accompanied by sublimation. There is one mode of decomposition which occurs at relatively high temperatures (∿300°C). This path for AP decomposition will not be discussed here as it does not occur at the temperatures of interest in the current program.

The mode of decomposition that is of most interest to the current program is that generally referred to as the low temperature (L.T.) decomposition. This is the decomposition which predominates at temperatures up to 300°C and which consumes 30% of the AP (after which time it ceases or continues at a very much reduced rate). Most AP decomposition studies have concerned themselves with this mode of decomposition however, ironically, it is the area of least consensus among the investigators.

Two processes occur in the low temperature regime, they are (a) sublimation and (b) slow decomposition. The sublimation process occurs by a dissociative evaporation process; there is no evidence for gaseous NH_4ClO_4 molecules. Both of these processes are stopped by NH_3 pressure and both appear to be predominantly surface phenomena. The surface area therefore can be expected to have a significant effect on the rates. Thus finally divided oxidizer will appear less stable.

There is evidence that low temperature decomposition is catalyzed by decomposition products and impurities and both L. T. Decomposition and sublimation produce products which oxidize the organic species of the binder. Aerojet's approach to oxidizer stabilization was based on understanding and controlling these factors.

Although subsequent studies at Aerojet have led to the development of far more effective stabilizers, the work with ANB-3289-2 propellant indicated that purification followed by treatment with FC-169 provided adequate stabilization to meet the heat sterilization requirement.

Binder Stability - Further evidence of the importance of oxidizer stabilization on propellant thermal stability is shown by the effect of 135°C (275°F) heat sterilization in air on the Shore hardness and weight loss of 2.5 cm (1 in.) propellant cubes of a standard state-of-the-art propellant. A very pronounced oxidizer-binder interaction is indicated by the extreme weight loss of 57% in 200 hr, that occurred in propellant prepared with standard ammonium perchlorate and an unsaturated hydrocarbon binder (Figure 36). This severe weight loss, which may represent an extreme case, is accompanied by an increase of 30 Shore "A" units of hardness. The weight loss, which primarily represents decomposition of ammonium perchlorate, is reduced to 0.2% after 360 hr storage (six, 60-hr cycles) by the use of a saturated hydrocarbon binder which is more stable to oxidation. A mild oxidative attack on the binder may be indicated by a Shore "A" hardness increase of 10 units. The use of stabilized ammonium perchlorate with the saturated binder produces the same weight loss and eliminates the change in Shore "A" hardness. The elimination of surface hardening by removing oxidative sites ensures that the propellant may be sterilized in air without degradation from air oxidation.

EFFECT OF 135°C (275°F) STORAGE ON THE SURFACE HARDNESS OF POLYBUTADIENE PROPELLANT

(2.5 cm (1 in) cubes)

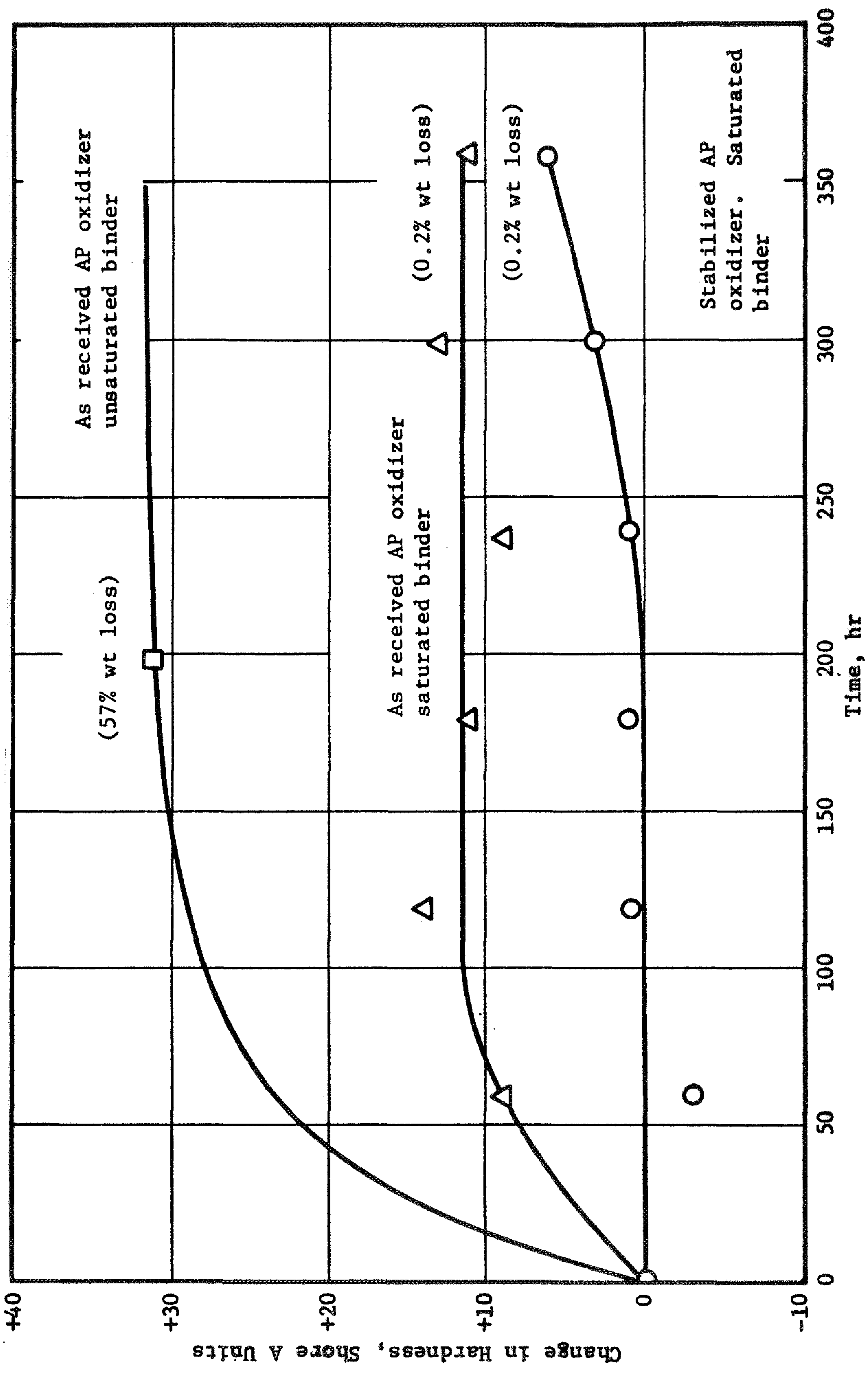


Figure 36

Processing - As shown in the foregoing discussion, valuable information on the stability of a formulation can be obtained from screening tests with one-inch propellant cubes. In tests with 7.6 x 7.6 x 12.7 cm specimens subjected to the long-term heat sterilization condition, it has been found that a stable binder and oxidizer are not the only criteria for the successful high temperature performance of a propellant grain. Minimization of voids or defects in the grain is also an absolute necessity. Small defects which may only be visible under magnification, and which have no apparent adverse effect on specimens stored at a more conventional temperature, e.g., 82°C (180°F), were found to enlarge progressively with each successive 135°C heating cycle. This behavior, apparently a manifestation of cumulative damage, probably results from application of a stress to the propellant at high temperature where its strength is low. Chemical changes, of course, may also be occurring at these elevated temperatures and cause an acceleration of the damage process. Diffusion path length, or web thickness is an important parameter for chemical degradation reactions involving gaseous products. Tests with specimens having small web thicknesses or short diffusion paths may not be totally indicative since gaseous products which may catalyze or promote degradation may escape more readily than from thicker webs.

The minimization of defects requires modifications in formulation and in the conventionally used propellant processing procedures. The modifications developed to obtain acceptable quality grains have been defined for ANB-3289-2 propellant and include (1) treating the propellant ingredients to eliminate volatile or mobile species prior to propellant mixing, (2) mixing under high vacuum, (<3mm Hg pressure), (3) casting with very efficient deaeration, (4) use of a hindered isocyanate to provide low viscosity and adequate pot life, and (5) adjustment of the crosslink density to provide propellant of a relatively high modulus.

The importance of low viscosity propellant with adequate potlife cannot be overemphasized. A rapid viscosity build-up precludes the casting of void-free grains. The use of dimeryl diisocyanate (DDI), a sterically hindered isocyanate, in place of such conventional isocyanates as tolylene diisocyanate in ANB-3289-2 propellant provides a 10 fold increase in pot life at 150°F (a change from 0.5 to 3 to 6 hr) with a viscosity at 3 hr of 900 N-sec/m (9000 poise) and a viscosity after 6 hr of 2000 N-sec/m (20,000 poise). This low viscosity combined with a reasonably long pot-life ensures the capability of casting high quality grains.

ANB-3289-2 propellant was processed using the critical modifications cited and a 7.5 x 7.5 x 12.5 cm (3 by 3 by 5-in.) block subjected to six 53-hr heat sterilization cycles at 135°C (275°F) in air. The effect of this heat treatment on the propellant mechanical properties is shown in Figure 37. The similarity in properties determined on specimens taken from the center and surface of the block attests to the excellent oxidative stability of the propellant as well as the absence of chemical and physical property changes in the interior. The significant effect of increased crosslink density in reducing the development of porosity from defect sites is shown. Tests with a similar propellant not processed in strict accordance with the above procedures showed that the block developed porosity which increased in degree after each heat cycle. Porosity was not observed in 2.5 cm cube tests.

EFFECT OF HEAT STERILIZATION ON THE MECHANICAL PROPERTIES OF ANB-3289-2 PROPELLANT

Batch No.	Cross-linker, Equiv.	History	Specimen Location	Porosity	Shore A Hardness	Mechanical Properties at 25°C (77°F)					
						σ_m		ε_m, %	ε_b, %	E_o	
						N/cm^2	(psi)			N/cm^2	(psi)
10LR-3563	30	Initial	--	Non-Porous	63	94	(136)	21	33	1179	(1708)
10LR-3563	30	Sterilized	Surface	Non-Porous	59	71	(102)	24	44	918	(1330)
10LR-3563	30	Sterilized	Center	Non-Porous	58	72	(104)	23	45	900	(1305)
10LR-3564	25	Initial	--	Non-Porous	57	81	(118)	36	68	609	(883)
10LR-3564	25	Sterilized	Surface	Non-Porous	50	53	(77)	34	63	466	(675)
10LR-3564	25	Sterilized	Center	Porous	47	47	(68)	29	38	493	(714)

Figure 37

APPENDIX B

DETERMINATION OF RELATIVE CHANGES IN THE STRESS-FREE TEMPERATURE

When a block of propellant is exposed to high temperatures for a period of time chemical reactions can take place within the polymeric binder. These reactions lead to polymeric chain scissions and chain linkages. If the block of propellant is mechanically deformed while at a high temperature, these chemical reactions become very important. For example, if a great number of polymer chains are broken, the propellant could flow and relieve the mechanically imposed stresses. But, in doing this the propellant block would have changed its shape. Now, if in this new shape additional chemical reactions occur to crosslink the polymeric chains then the new shape could be considered to be permanently established. In actuality, polymeric chain scissions and chain crosslinking take place essentially simultaneously and in varying amounts depending upon the chemical nature of the system.

For a case-bonded propellant grain the effect is seen as follows. The propellant, after casting, is cured at some temperature, say T_c. If we can ignore cure shrinkage then we can say that the grain is stress-free except for gravitational loads. Thus, T_c becomes the stress-free temperature, T_{sf} (in actuality, because of the cure shrinkage T_{sf} is above T_c by a small amount). Now, if the propellant is heated to some higher temperature, T_h, the grain will change shape because of interactions with the case. If the chemical reactions noted above take place, then the grain would take on this new shape, the stresses (non-gravitational) would fall to zero and T_h would become the new stress-free temperature.

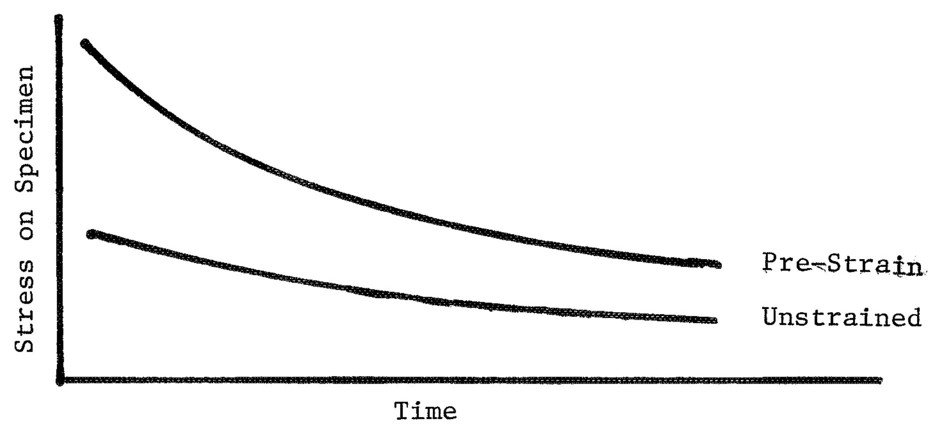
In practice, the chemical reactions are not extensive so the change in shape and changes in the stress-free temperature are only partially accomplished. That is, the T_{sf} increases, but not to T_h. Also, a permanent change in shape does occur, but it is intermediate between those observed at T_c and at T_h.

To determine where the intermediate value of T_{sf} occurs requires the measurements of grain stresses while the grain is exposed to various temperatures. T_{sf} is that temperature where the thermal stresses fall to zero. In practice, these measurements on motors are difficult and expensive to run. In their place it is recommended that we evaluate changes in T_{sf} using simple measurements on propellant blocks.

This test is easily performed and allows a number of variations. A bulky specimen is recommended. Thus, a specimen, 5 cm diameter by 12.5 cm (2 in. x 5 in) might be used. Metal plates would be bonded to both ends and the overall dimensions determined.

One set of specimens would be stored at the desired high temperature without load; while a second set of specimens would be placed under a 5% (arbitrary) compression and stored at the desired temperature for the required period. At the end of this period the specimens would be returned to room temperature and held for at least 48 hours for thermal equilibration.

At this point, the two sets of specimens would be pulled to a 5% (arbitrary) strain (based on the original length) and the stresses monitored as in a stress relaxation test. The two relaxation curves should appear roughly as shown below.



After a time the stress on the unstrained specimens, σ_u, would be given approximately by*

$$\sigma_u \approx E_e \varepsilon \tag{A-1}$$

where ε is the strain imposed during the test.

The stress on the pre-strained specimen, σ_p, would be given approximately by*

$$\sigma_p \approx E_e(\varepsilon - f\varepsilon_p) \tag{A-2}$$

where ε_p is the imposed pre-strain

f is the fractional change in the grain shape during the high temperature storage.

The fraction f is related to T_{sf} as follows

$$f = \frac{T_{sfn} - T_{sfo}}{T_h - T_{sfo}} \tag{A-3}$$

where T_{sfn} is the new stress-free temperature

T_{sfo} is the original stress-free temperature

T_h is the high temperature where the specimens were stored

Taking the ratio of Equation (A-2) to (A-1) and solving for f we obtain

$$f = \frac{\varepsilon}{\varepsilon_p}\left(1 - \frac{\sigma_p}{\sigma_u}\right) \tag{A-4}$$

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* The purpose for heating both sets of specimens to high temperatures is to eliminate the effect of variations in the crosslink density which would modify E_e. When both sets of specimens are heated the value of E_e should be the same for both Equations (A-1) and (A-2).

Combining Equations (A-3) and (A-4) gives

$$T_{sfn} = T_{sfo} + \frac{\varepsilon}{\varepsilon_p} \left(1 - \frac{\sigma_p}{\sigma_u}\right) (T_h - T_{sfo}) \tag{A-5}$$

The value of T_{sfo} would be estimated from the cure temperature together with cure shrinkage data for the grain.

Equation (A-5) yields the empirical value for T_{sfn} for a block of propellant heated from room temperature. It is expected that other starting temperatures (providing no serious chemical effects occur) would yield essentially the same values.

Tests of this type need to be developed and confirmed by direct experiments on motors. A number of factors which can influence T_{sf} measurements also require consideration. The variations in T_{sf} may well be many times more important than <u>all</u> of the factors currently being considered in surveillance studies and grain structural integrity analyses.

APPENDIX C

APPARATUS, EQUIPMENT AND MEASUREMENT PROCEDURE USED IN HEAT STERILIZATION TESTING

HEAT STERILIZATION OVEN

Hotpack, Model 1302 Air Circulating Oven

TEMPERATURE MONITORING

Continuous with Honeywell-Brown Strip Chart Recorder - Type J Thermocouple

TEMPERATURE VARIATION AS RECORDED

Cycles 1,3,4,5 and 6. Temperature fluctuated between 135.0 and 136.6°C (275 - 278°F) Cycle 2 apparently due to a power fluctuation temperature cycled between 132.2 and 135.0°C (270-275°F).

BORE MEASUREMENTS

Measurements 0.5 cm from each end and at center of grain with Brown and Sharpe INTRIMIK.

RADIOGRAPHIC EXAMINATION

Two X-rays of each motor were taken to establish bond integrity and void or crack formation. The views represented an initial view and a second view in which the motor had been rotated 90°.

BIBLIOGRAPHY

(1) Robillard, C. L., Dowler, W. L., Shafer, J. I., Udlock, D. E., Heat Sterilizable Solid Propellants, NASA-TR-32-1187, 1967.

(2) Weinberg, L., Demonstration of a Sterilizable Solid Propellant Rocket Motor, NASA-CR-111772, 1970 (United Technology Center).

(3) Bircumshaw, L. L., and Newman, B. H., Proc. Royal Soc., 41, 227-228, (1955).

ACKNOWLEDGEMENTS

The following persons contributed significantly to the success of the demonstration program and should be acknowledged for their contribution.

G. A. Zimmerman - the suggestion and design of the stress relieved motor.

J. D. McConnell and R. N. Shearly - stress analysis

K. W. Bills - aid in understanding and dealing with the limitations of conventional stress analysis, and suggestion of the method for prediction of stress-free temperature changes.